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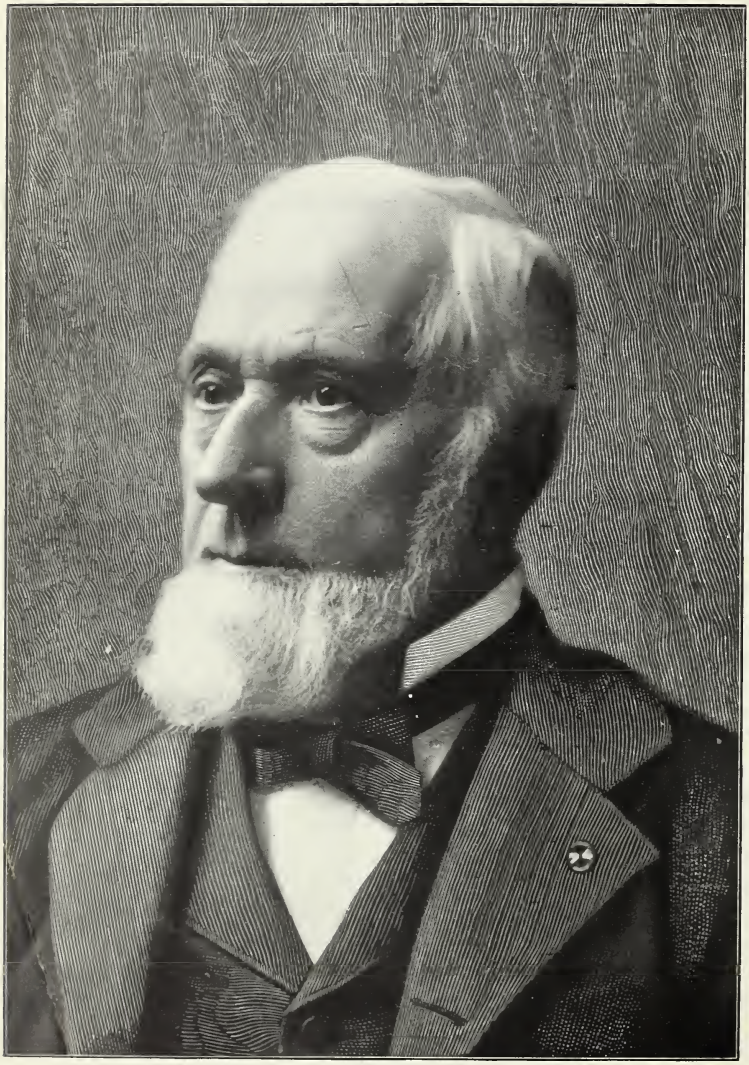


R. A. Kedzie

U. S. DEPARTMENT OF AGRICULTURE.

BUREAU OF CHEMISTRY—BULLETIN NO. 73.

H. W. WILEY, Chief of Bureau.

PROCEEDINGS

OF THE

NINETEENTH ANNUAL CONVENTION

OF THE

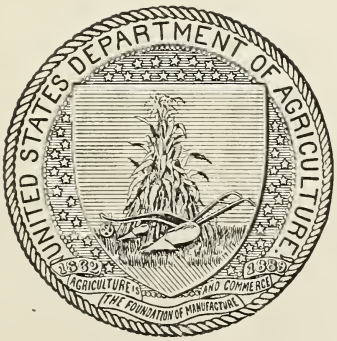
ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS,

HELD AT

WASHINGTON, D. C., OCTOBER 2, 3, AND 4, 1902.

EDITED BY

HARVEY W. WILEY,
SECRETARY OF THE ASSOCIATION.



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1903.

LETTER OF TRANSMITTAL.

U. S. Department of Agriculture,
Bureau of Chemistry,
Washington, D. C., December 15, 1902.

Sir: I have the honor to transmit herewith the manuscript of the proceedings of the nineteenth annual meeting of the Association of Official Agricultural Chemists, with the request that it be published as Bulletin No. 73 of this Bureau.

H. W. Wiley,
Chief of the Bureau of Chemistry and Secretary of the Association of Official Agricultural Chemists.

Hon. James Wilson,
Secretary of Agriculture.

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PROCEEDINGS OF THE NINETEENTH ANNUAL CONVENTION OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS.

FIRST DAY.

THURSDAY—MORNING SESSION.

The nineteenth annual convention of the Association of Official Agricultural Chemists was called to order by President H. J. Wheeler at 10 o'clock on the morning of October 2, 1902, in the lecture hall of the Columbian University. The following members and visitors were in attendance during the sessions of the convention:

MEMBERS AND VISITORS PRESENT.

Allen, Edwin W., U. S. Department of Agriculture, Washington, D. C.
Angelo, Oliver Perry, U. S. Department of Agriculture, Washington, D. C.

Bache, Arthur Wilbur, U. S. Department of Agriculture, Washington, D. C.
Barnard, Harry E., Chemist State Board of Health, Concord, N. H.
Beal, W. H., U. S. Department of Agriculture, Washington, D. C.
Bigelow, W. D., U. S. Department of Agriculture, Washington, D. C.
Bisbee, Derward B., City Chemist, 7340 Bond avenue, Chicago, Ill.
Blouin, Robert E., Agricultural Experiment Station, Audubon Park, New Orleans, La.
Bosworth, Alfred W., Agricultural Experiment Station, Kingston, R. I.
Breazeale, James F., U. S. Department of Agriculture, Washington, D. C.
Brooke, John C., U. S. Department of Agriculture, Washington, D. C.
Browne, Charles A., jr., Sugar Experiment Station, Audubon Park, New Orleans, La.
Burd, John S., U. S. Department of Agriculture, Washington, D. C.

Chace, E. M., U. S. Department of Agriculture, Washington, D. C.
Carpenter, Frank B., Virginia-Carolina Chemical Company, Richmond, Va.
Carroll, John S., Agricultural College, Miss.
Cavanaugh, George W., Cornell University Agricultural Experiment Station, Ithaca, N. Y.
Chamberlain, Joseph S., U. S. Department of Agriculture, Washington, D. C.
Craighill, George P., John H. Heald & Co., Lynchburg, Va.
Crampton, C. A., Treasury Department, Washington, D. C.

Davidson, R. J., Agricultural Experiment Station, Blacksburg, Va.
Donk, Marion G., Assistant State Chemist, Tallahassee, Fla.
Doyle, Aida M., U. S. Department of Agriculture, Washington, D. C.
Dubois, Wilbur L., U. S. Department of Agriculture, Washington, D. C.

Eaton, Edward N., State Analyst, 1628 Manhattan Building, Chicago, Ill.
Ewell, E. E., U. S. Department of Agriculture, Washington, D. C.

Fraps, George S., Agricultural Experiment Station, Raleigh, N. C.
Frear, William, Agricultural Experiment Station, State College, Pa.

Gore, Herbert C., U. S. Department of Agriculture, Washington, D. C.
Goss, Ralph M., U. S. Department of Agriculture, Washington, D. C.
Gough, T. R., Maryland Agricultural College, College Park, Md.

Hamilton, John, Secretary of Agriculture of Pennsylvania, State College, Pa.
Howard, Burton J., U. S. Department of Agriculture, Washington, D. C.
Harcourt, Robert, Ontario Agricultural College, Guelph, Ontario, Canada.
Hart, E. B., Agricultural Experiment Station, Geneva, N. Y.
Haskins, Henri D., Massachusetts Agricultural College, Amherst, Mass.
Haywood, John K., U. S. Department of Agriculture, Washington, D. C.
Herff, B. von, Director of German Kali Syndicate, New York, N. Y.
Hite, Bert H., Agricultural Experiment Station, Morgantown, W. Va.
Holmes, Charles W., The Columbian University, Washington, D. C.
Hopkins, Cyril G., Agricultural Experiment Station, Urbana, Ill.
Houghton, Harry W., U. S. Department of Agriculture, Washington, D. C.

Jaffa, Myer E., Agricultural Experiment Station, Berkeley, Cal.
Jenkins, Edward H., Agricultural Experiment Station, New Haven, Conn.
Jones, Charles H., Agricultural Experiment Station, Burlington, Vt.

Knight, Carlisle P., U. S. Department of Agriculture, Washington, D. C.
Krug, William H., U. S. Department of Agriculture, Washington, D. C.

La Bach, James O., Agricultural Experiment Station, Lexington, Ky.
Langworthy, C. F., U. S. Department of Agriculture, Washington, D. C.
Lansdale, Harry N., Assistant State Chemist, College Park, Md.
Lawson, H. W., U. S. Department of Agriculture, Washington, D. C.
Leach, Albert E., State Board of Health, Boston, Mass.

McCandless, John M., State Chemist, Atlanta, Ga.
McCarthy, Eugene R., U. S. Department of Agriculture, Washington, D. C.
McDonnell, Curtis C., Agricultural Experiment Station, Clemson College, S. C.
McDonnell, Henry B., Agricultural Experiment Station, College Park, Md.
Magruder, Egbert W., Department of Agriculture, Richmond, Va.
Meng, James S., German Kali Works, 93 Nassau street, New York, N. Y.
Mooers, Charles A., Agricultural Experiment Station, Knoxville, Tenn.
Moore, Charles C., U. S. Department of Agriculture, Washington, D. C.
Morrison, William G., F. S. Royster Guano Company, Norfolk, Va.
Morse, Fred W., Agricultural Experiment Station, Durham, N. H.
Munroe, Charles E., Columbian University, Washington, D. C.
Munson, Lewis S., U. S. Department of Agriculture, Washington, D. C.

Needham, Charles W., The Columbian University, Washington, D. C.
Norton, John H., U. S. Department of Agriculture, Washington, D. C.

Oshima, Kintaro, Middletown, Conn.

Page, Logan Waller, U. S. Department of Agriculture, Washington, D. C.
Patrick, George E., U. S. Department of Agriculture, Washington, D. C.
Patterson, Henry J., Agricultural Experiment Station, College Park, Md.
Penny, C. L., Agricultural Experiment Station, Newark, Del.
Price, Thomas M., Agricultural Experiment Station, College Park, Md.

Reed, Herbert C., Stamford Manufacturing Company, Stamford, Conn.
Robb, John B., Agricultural Experiment Station, College Park, Md.

Ross, B. B., State Chemist, Auburn, Ala.
Runyan, E. G., Inspector of Gas and Meters, Washington, D. C.

Sawyer, Harris E., Consulting Chemist, Boston, Mass.
Seidell, Atherton, U. S. Department of Agriculture, Washington, D. C.
Smith, Bernard H., U. S. Department of Agriculture, Washington, D. C.
Smith, Joseph G., U. S. Department of Agriculture, Washington, D. C.
Spencer, Guilford L., U. S. Department of Agriculture, Washington, D. C.
Stewart Andrew, U. S. Department of Agriculture, Washington, D. C.
Street, John P., Agricultural Experiment Station, New Brunswick, N. J.
Stuart, Duncan, U. S. Department of Agriculture, Washington, D. C.

Teas, William H., Ridgway, Pa.
Terne, Bruno, Union Abattoir Company, Baltimore, Md.
Tolman, L. M., U. S. Department of Agriculture, Washington, D. C.
Trescot, T. C., U. S. Department of Agriculture, Washington, D. C.

Van Slyke, Lucius L., Agricultural Experiment Station, Geneva, N. Y.
Veitch, H. P., U. S. Department of Agriculture, Washington, D. C.

Warner, Harry J., U. S. Department of Agriculture, Washington, D. C.
Watts, Henry C., 850 Drexel Building, Philadelphia, Pa.
Wheeler, H. J., Agricultural Experiment Station, Kingston, R. I.
Wiley, H. W., U. S. Department of Agriculture, Washington, D. C.
Williams, Charles B., Department of Agriculture, Raleigh, N. C.
Wilson, James, Secretary of Agriculture, Washington, D. C.
Wilson, Nathaniel E., Agricultural Experiment Station, Reno, Nev.
Wilson, Herman T., Buena Vista Extract Company, Buena Vista, Va.
Winton, A. L., Agricultural Experiment Station, New Haven, Conn.
Woods, C. D., Agricultural Experiment Station, Orono, Me.

The following order of business was followed:

ORDER OF BUSINESS.

The president's address.
Reports of the referees in the following order:

1. Report on nitrogen.
2. Report on potash.
3. Report on phosphoric acid.
4. Report on soils.
5. Report on ash.
6. Report on foods and feeding stuffs.
7. Report on food adulteration.
8. Report on dairy products.
9. Report on sugar.
10. Report on tannin.
11. Report on insecticides.
12. Reports of special committees (food standards, fertilizer legislation).

The president addressed the convention as follows:

PRESIDENT'S ADDRESS.

Gentlemen of the Association of Official Agricultural Chemists: An unwritten law seems to have come into existence to the effect that the president of this association is expected to deliver a more or less formal address upon the opening of the convention.

Owing to the fact that new and somewhat arduous executive duties have been added, temporarily, to those which fall to my regular lot, it was but natural that I should seek some precedent for the omission of such an address. It was, therefore, with a feeling of intense satisfaction that I discovered in reading the early records of this association that presidential addresses were not at first in vogue. In fact every president of the association who has been troubled to find the time to prepare a formal address, or who has felt that the grain has already been thrashed from the association "straw," has good reason to place the burden of his complaint upon the shoulders of our present secretary, Mr. Wiley, who, so far as the records show, seems to have been the first president to "address" the association. This address was delivered upon the occasion of the opening of the third convention. Upon the opening of the fifth convention President Chazal omitted the address, since, as he said, "there was a desire to proceed at once to business with the view of accomplishing the objects of the convention in as short a time as possible." Upon the opening of the sixth convention such an excellent address was delivered by our late esteemed friend, John A. Myers, that the custom became firmly established. In lieu of a formal address I shall merely call attention to a few matters which it may be well for us to consider at this time.

Upon reading the proceedings of the eighteenth convention, attention is attracted to several important changes in the methods of business previously in vogue. As a necessary result of the expansion of our work the methods of the "town meeting" have gradually given place to those of a parliamentary body.

Perhaps the most important improvement is the appointment of several committees on "recommendations of referees" instead of a single committee. The results of this change are so gratifying and the necessity of it so obvious to all, that there seems to be little chance that the system will be changed in the near future except by adding new committees as the volume and the character of the work may demand. According to the vote passed at the last convention this committee can only be called upon at this session to report upon minor matters. Important recommendations by referees, such as the adoption of new methods or the radical change of old ones, may be considered by the committees at their leisure, instead of under pressure as heretofore, and the final report is to be rendered, in printed form,

if possible, to each member of the association as soon as convenient after the close of the present session. Final action upon the report of these committees can then be taken at the next succeeding convention, or after ample time has been given to all to fully consider and test the proposed changes.

Several important modifications of the constitution, which were made in 1901, were necessitated by the great expansion of the work undertaken, and may be looked upon as the milestones marking the association's path of progress.

It is doubtful if any single point is of greater moment than for us to keep continually in mind that we exist for the purpose of improving and perfecting our methods of analysis, and not for the purpose of testing the work of individual chemists. The older members of the association can readily recall times when this point was seemingly forgotten by referees, to the great detriment of our work.

It can not be too often reiterated that several States in the Union have incorporated in their laws a provision that the results secured by the official methods of this association shall be accepted as final evidence in the courts of the respective States. For this reason as well as from motives of pride in our association we should not be influenced in the adoption and modification of methods solely by the desire to secure an official sanction to some scheme of analysis which will enable us to do our work more quickly or easily, but should exercise due care and act conservatively.

Owing to the complex character of certain investigations undertaken by the association, and the fact that a considerable amount of original research is sometimes demanded, the appointment of a committee to deal with certain subjects rather than a referee and an associate, would seem to be worthy of consideration. It is not infrequently the case that the member of the association who would naturally be selected as referee or associate referee by virtue of his special experience, is too fully occupied to give the matter the attention which is demanded of a referee under the present system. The advice of such a member might, however, be invaluable in formulating lines of investigation and his service might be secured upon such a committee where he might act solely in an advisory capacity.

In connection with the study of methods great attention should be paid in many instances to fundamental principles which tend to affect the final results. As instances of this one might cite the necessity of a careful study of the conditions and circumstances affecting the composition of the "yellow precipitate" obtained in connection with the volumetric determination of phosphoric acid, also the desirability of perfecting methods for the more satisfactory differentiation of the phosphoric acid of soils.

Since the last convention, Congress has officially recognized this

association by making it adviser to the Secretary of Agriculture in all matters relating to food standards.

As a result of several inquiries regarding Battle and Dancy's chemical conversion tables, it has been ascertained that the tables are now out of print and that the authors have no intention of issuing a new edition. They have expressed their willingness to have this association make such use of the tables as it desires provided due credit is given to the authors. As a matter of convenience to our members it is recommended that the association consider the advisability of publishing the same or a similar and more comprehensive set of tables for general laboratory use.

Let us in beginning our labors for another year not waste our energies in congratulating ourselves upon the work of the past, but rather look forward to still further energetic and harmonious action, such as has ever tended to enhance the value of our work in the past.

APPOINTMENT OF COMMITTEES.

The PRESIDENT. If I mistake not, the announcement of committees is now in order. It gives me pleasure to appoint the following committee to wait upon the Secretary and Assistant Secretary of Agriculture for the purpose of inviting these gentlemen to attend our meeting:

Messrs. Jaffa, Davidson, and Jenkins.

Committee on resolutions: Messrs. Van Slyke, Frear,[a] and Ross.

Committee on nominations: Messrs. Bigelow, Street, and Jones.

In regard to the committee on nominations, I would like to say that it seems desirable that the election of officers take place, if possible, to-morrow forenoon in order that the executive committee may have time to appoint the referees for next year and announce them before the close of the convention. I would therefore like to suggest that the committee on nominations be asked to report, if possible, to-day, and that we make the election a special order for to-morrow forenoon in order that this may be accomplished.

Committee on amendments to the constitution: Messrs. Frear,[b] Hite, and Hopkins.

I would like to ask if it is the pleasure of the association that the same number of members be appointed on the committees on recommendations of referees as last year. The association will remember that prior to last year we had but one committee on recommendations of referees. Last year a special committee was appointed to propose a subdivision of the subjects. This committee subdivided the work under Committees A, B, and C, Committee A having in charge phosphoric acid, potash, nitrogen, soils, ash, and insecticides; Committee B, dairy

[a] Mr. H. B. McDonnell was later appointed in the place of Mr. Frear.

[b] Mr. Van Slyke was afterwards appointed in the place of Mr. Frear.

products, foods and feeding stuffs, and tannin;[a] and Committee C, food adulteration. Is it the desire of the association that the committees be modified this year, or that they shall remain the same? I should be glad to hear some expression of opinion on this question and await your pleasure as to a motion.

Mr. DAVIDSON. I move that the same committees be appointed. I think they helped very much in the dispatch of business.

The motion was carried, and the president appointed the following: Messrs. Street, Jaffa, Veitch, Ross, and Runyan, on Committee A; Messrs. Krug, C. A. Browne, Haskins, Munson, and C. H. Jones, on Committeee B, and Messrs. Leach, Winton, Eaton, Barnard, and Tolman on Committee C.

Mr. WILEY. Mr. President, I would like to move that the committee on invitations include the names of the president of this university, Dr. Needham, who was appointed a few months ago, and the dean of the Graduate School, Dr. Munroe. Through their courtesy we are occupying this building, and I think they would appreciate the compliment of an invitation to attend some of our sessions.

The motion was carried, and the committee was instructed to act accordingly.

The PRESIDENT. According to our order of business, the first report to be given is that on nitrogen. Word has been received that the referee on nitrogen will not be here until 10.30 a. m. If it is agreeable to the association we will pass on to the report on potash.

Mr. WILEY. Mr. President, before proceeding with the regular order of business, I would like to say in regard to the committee on food standards that Mr. Frear, the chairman of that committee, is compelled to go away to-night, therefore I move that the report of this committee be received this afternoon.

The motion prevailed.

On motion of Mr. Wiley, the election of officers was set for 11 o'clock Wednesday morning.

Mr. WILEY. I would like to say that the Cosmos Club has extended the courtesy of the club to the members of this association during their stay in the city. The club is on the corner of H and Sixteenth streets, and you will be welcomed there. On entering please register your name in the book, so that we may have a record of those who attend.

The PRESIDENT. It is also with regret that I am obliged to announce that the report of the referee on potash is not ready. It can be presented this afternoon. The next in order will be the report on phosphoric acid.

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[a] Sugar should have been included in the work of this committee.

REPORT ON PHOSPHORIC ACID.

By C. H. Jones, *Referee.*

Your referee on phosphoric acid has been unable to give the subject delegated to his keeping the attention he desired owing to pressure of work connected with fertilizer and feeding-stuff inspections coming at a time when the preliminary work of formulating trial methods for this year's work should have been done.

Fortunately, however, the total phosphoric acid work has received such careful attention in the past by this association that the methods are in a satisfactory shape and need no overhauling at a referee's hands. The method for the determination of available phosphoric acid is not in as good favor. While ammonium citrate serves fairly well with acid goods it affords low results of doubtful validity with basic slag. Some demand has therefore arisen for a change in the present method of determining the available phosphoric acid content of basic slags. This demand doubtless led your last referee to suggest that further study along these lines was in order.

Contemplated changes from the official method fall naturally into two classes: (1) The substitution for ammonium citrate of another solvent that will be of more general application; (2) the adoption of special solvents for special phosphatic materials. The pros and cons of this question have all been brought to your attention during past sessions and do not merit further attention here.

At the 1900 meeting of this association Mr. Thomas Macfarlane submitted a scheme of citric-acid treatment applicable to commercial fertilizers and a modification of the same fitted for use with basic slag, ground bone, etc. This method is outlined in Bulletin No. 62, Bureau of Chemistry, U. S. Department of Agriculture (p. 50), as well as in Bulletin No. 75 of the inland revenue department, Ottawa, Canada. Mr. Macfarlane shows that different basic slags carry varying amounts of free lime, and that if this be removed before treatment by any method for availability an increased solubility of the phosphoric acid apparently results. He suggests the use of ammonium chlorid solution to remove this lime, and further shows that such treatment does not dissolve the phosphoric acid compounds. These methods are now in use in Canadian fertilizer inspection laboratories, and the results obtained by their use are shown in Bulletins Nos. 75 and 81 of the inland revenue department, Ottawa, Canada. As a rule the so-called insoluble phosphoric acid content is decreased, and consequently that of the citric soluble and available phosphoric acids is increased, particularly in bone fertilizers and slags.

The referee for 1901 was instructed to investigate along these lines. His report contains the results obtained by a citric-acid process, details of which can be seen in Bulletin No. 67, Bureau of Chemistry, U. S. Department of Agriculture (p. 23). The removal of lime by ammonium chlorid solution was, however, not mentioned.

The report of the referee for 1897 also contains the results of comparisons of different methods for determining the availability of basic slag, including modifications of the present ammonium citrate method, Wagner's method, and a 1 per cent citric-acid method.

During the time at his disposal your referee has obtained a few results by different methods, which are here presented:

Phosphoric Acid in Basic Slag.

	Per cent.
1. Total phosphoric acid found	17.56
Available phosphoric acid found by—	
2. Direct treatment "official" ammonium citrate method	5.22
3. Substituting 100 cc 1 per cent citric acid for ammonium citrate	4.72
4. Substituting 100 cc 2 per cent citric acid for ammonium citrate	7.21
5. Substituting 100 cc ammonium citrate+100 cc water	4.54

				Per cent.
6.	Washing 2 grams on filter with 200 cc water.		Residue treated as per (2)	6.94
7.			Residue treated as per (5)	7.00
8.			Residue treated as per (3)	4.98
9.			Residue treated as per (4)	8.17
10.	Washing 2 grams on filter with 200 cc 5 per cent sugar solution.		Residue treated as per (2)	6.44
11.			Residue treated as per (5)	6.80
12.			Residue treated as per (3)	5.74
13.			Residue treated as per (4)	8.93
14.	Washing 2 grams on filter with 200 cc 5 per cent ammonium chlorid solution.		Residue treated as per (2)	6.89
15.			Residue treated as per (5)	7.36
16.			Residue treated as per (3)	6.63
17.			Residue treated as per (4)	9.06
18.	Boiled 2 grams with 100 cc 5 per cent ammonium chlorid solution, replacing evaporated water.		Residue treated as per (2)	8.70
19.			Residue treated as per (3)	7.40
20.			Residue treated as per (4)	9.14
21.	Rotated 30 minutes with 200 cc.	Water (room temperature), 5 per cent ammonium chlorid.	Residue treated as per (2)	7.22
22.			Residue treated as per (2)	8.04
23.	Macfarlane method.	Boil 2 grams with 100 cc 5 per cent ammonium chlorid solution. Filter. Add to residue 100 cc 1 per cent citric acid. Shake. Add 100 cc more 1 per cent citric acid. Shake every five minutes for half an hour. Filter; wash. Determine phosphoric acid in residue.	Temperature, 20° C	10.44
24.			Temperature, 30° C	10.51
25.			Temperature, 40° C	10.90
26.			Temperature, 50° C	10.75

The results, it is seen, run from 4.54 per cent to 10.90 per cent, depending on the method of procedure. With the Macfarlane method the variation in results between 20° and 50° C. is not marked, and indicates that differences in ordinary room temperatures have only a slight influence. The last four results were obtained by difference between the total phosphoric acid present and that remaining in the insoluble residue. The direct percentages obtained by determining the phosphoric acid in the filtrate were 10.36, 10.83, 11.06, and 10.88, respectively. They show fair agreement, and a direct estimation would often save considerable time.

On boiling 2 grams of this slag in 100 cc of 5 per cent ammonium-chlorid solution for thirty minutes and replacing evaporated water, there was removed 11.87 per cent of lime (CaO). Boiling in 200 cc of a similar solution removed 13.35 per cent of lime (CaO). No phosphoric acid was found in the filtrates from the above. Washing 2 grams on a filter with 200 cc of the ammonium chlorid solution removed 6.42 per cent of lime, while a similar washing with 5 per cent sugar solution dissolved only 1.85 per cent of lime. The sample sent out by the referee in 1901 gave an availability of 11.57 per cent by the Macfarlane method.

It is well recognized that the solvent power of the sundry solutions employed in availability determinations depends upon the quantity of the solvent and material used and the length of time allowed for its action. Temperature also plays its part. This being true, it would seem desirable to at least agree on the per cent of the total phosphoric acid present we are willing to concede as available in a sample of basic slag of standard composition and fineness. For example, let us say that the Wagner method shows 80 per cent available phosphoric acid and the present ammonium citrate method 30 per cent. There may be those present who believe the former is too high, while I think we are all agreed that the latter is too low. The happy medium therefore lies between 30 and 80 per cent, and if once agreed upon it would, in my opinion, prove of great help in the selection of a special method for the availability of phosphoric acid in basic slag.

The PRESIDENT. Before proceeding to the next subject I would like to announce changes in committees necessitated by Mr. Frear's being called away. I appoint in his place Mr. McDonnell, on the committee on resolutions, and as chairman of the committee on amendments to the constitution, Mr. Van Slyke. Next in order will be the report on ash.

REPORT ON ASH.

By G. S. FRAPS, *Referee.*

Before sending out samples or requests for cooperation the referee undertook the following work on the determination of sulphur:

PRELIMINARY WORK ON SULPHUR.

The following methods were studied:

(1) *Nitric-acid method (the provisional method of the association).*

Five grams of material are placed in a 3½-inch porcelain evaporating dish, 20 cc of nitric acid (concentrated) added, and the mixture heated cautiously on the water bath until all danger of overflowing has passed. It is then partly evaporated, 10 cc of a 5 per cent solution of potassium nitrate is added, the mixture evaporated to complete dryness, and ignited, at first gently, then under a blast lamp until the residue is white. It is then dissolved in hydrochloric acid, evaporated to dryness, and heated for some time in an air bath to render silica insoluble. The residue is taken up in water with the addition of a little acid, filtered, and the sulphuric acid precipitated with barium chlorid in the usual way.

This method gives good results. It has a disadvantage, however, in that the ash produced is easily fusible, acts upon the porcelain dish, and is ignited free of carbon with great difficulty. It was to overcome this objection that the modification described below was tested.

(2) *Nitric-acid method modified.*

The modification consists in the use of 20 cc of a solution of calcium acetate containing 0.56 gram of calcium oxid (CaO), in place of 20 cc of potassium-nitrate solution. The ignition takes place much more easily, the ash does not fuse, and is more easily burned free of carbon than when potassium nitrate is used.

(3) *Boiling with nitric acid.*

An attempt was made to destroy the organic matter by boiling the material with nitric acid, which I understand is the method used for meats in the nutrition investigations of the Office of Experiment Stations. The method did not succeed with vegetable materials. Several experiments were made, but in no case was all organic matter of the vegetable materials destroyed, even when 5 grams of material was boiled to dryness with 100 cc nitric acid in a Kjeldahl flask. As it would, therefore, be necessary to wash the residue from the flask into a dish, and ignite with the addition of potassium nitrate or calcium acetate to remove organic matter, this method would differ from the two preceding only in that a larger quantity of acid is used and the digestion with the acid is more prolonged. The method was not further examined.

(4) *Fusion with caustic soda.*

This is the standard method for determining sulphur in nonvolatile organic compounds. The method as tested was as follows:

Five grams of material in a nickel crucible were saturated with 40 cc of a solution

of 150 grams sodium hydroxid in 300 cc water, evaporated to dryness, and fused with the addition of a little sodium peroxid. The fusion requires care to prevent the material from overflowing the dish, and the whole process is somewhat long. The melt was dissolved in water, neutralized and acidified with hydrochloric acid, evaporated to dryness and heated to render silica insoluble, filtered, and the sulphuric acid precipitated from the filtrate, the volume of which was about 200 cc. The sodium hydroxid and sodium peroxid contained a large quantity of sulphates; about 0.1 gram in the quantity used in the determination was found in the blank determination. The results with this method are decidedly low. This may possibly be due to the solubility of barium sulphate in sodium chlorid, about 38 grams of the latter salt being present in the solution from which the barium sulphate was precipitated, or it may be owing to the error caused by impurities in the reagents.

(5) *Eschka's method.*

This is the method usually employed for the determination of sulphur in coals. It was applied to plant materials as follows:

Five grams material were intimately mixed, in a platinum dish, with $7\frac{1}{2}$ grams of a mixture of two parts magnesium oxid to one of dried sodium carbonate. The mixture was heated, stirring frequently, and the temperature raised slowly until all carbon appeared to be burned off. The mass was transferred to a beaker with about 50 cc water; 15 cc of saturated bromin water was added and boiled five minutes. It was allowed to settle, decanted through a filter, boiled a second and third time with about 30 cc water, and washed thoroughly. The filtrate was made acid with hydrochloric acid, boiled until bromin was expelled, and then precipitated with barium chlorid in the usual way. The results by this method were too low.

RESULTS OF WORK.

The analytical results by the different methods are given in the following table (Table I). The figures in each case are corrected for the sulphur in the reagents found by a blank determination. The blank was very low in the case of the two nitric-acid methods. In the Eschka method it was equivalent to 0.0058 gram barium sulphate in the quantity of the reagents used for each test. As has already been stated, the fusion method gave results much too low, and the blank was high, being 0.1103 gram barium sulphate.

TABLE I.—*Determination of sulphur (SO_3) by different methods.*

	Nitric-acid method.	Nitric-acid method modified.	Eschka method.
	Per cent.	*Per cent.*	*Per cent.*
Corn	0.249	0.287	0.238
	.244	.286	.208
Average	.247	.287	.223
Peas	.481	.480	.297
	.533	.....	.312
	.503	.....	.313
Average	.518	.480	.307
Millet	.369	.427	.451
	.376	.434	.460
	.400	.....	.....
Average	.382	.431	.456

Official Work on Sulphur.

It was decided to compare the provisional method for the determination of sulphur with the method modified by the use of calcium acetate in place of potassium nitrate. A comparison between two methods for potash was also determined. The following circular letter was sent out to a number of members of this body:

Raleigh, N. C., *May 1, 1902.*

Dear Sir: The referee on ash for the present year will continue the study of the methods of determining sulphur and potash in plant materials. It is thought best to work out one portion of the problem at a time. Kindly inform the referee if you will be able to cooperate. The samples will be sent out about the latter part of May. The work of last year proves conclusively that the sulphur in an ash, as ordinarily prepared, is no indication of the amount of sulphur in the plant, which may be vastly greater. Kindly give us the benefit of any suggestions.

Very truly,

G. S. Fraps, *Referee.*
Frank T. Shutt, *Associate Referee.*

Eight chemists requested samples. R. J. Davidson, of Virginia, sent the following table of analyses:

Table II.—*Determination of sulphur (SO_3) by different methods (Davidson).*

Method.	Dried apples, sample 1.	Dried apples, sample 2.	Bran.
	Per cent.	*Per cent.*	*Per cent.*
Ignition with calcium acetate	0.09	0.10	0.27
Nitric-acid method	.09	.10	.45
Eschka's method	.10	.11	.....
In ash	.....	.....	.09

W. P. Headden, of Fort Collins, Colo., wrote as follows:

If you will refer to my bulletin on alfalfa, No. 35, of this station, pages 84–87, you will see that I did some work in this line in 1895 in regard to chlorin, sulphur, and phosphorus, but did nothing in regard to loss of potash. I found a very considerable loss of chlorin and sulphur, but none for phosphoric acid. I was rather surprised at the latter, as we know that phosphates heated with carbon, especially if there is sand enough present to set phosphoric acid free, may be reduced. In my experiments there were doubtless enough basic salts present to avoid such reactions; besides, the temperature of incineration was very low—as low as would accomplish the incineration.

You state that the sulphur in the plant may be vastly greater than that indicated by the determination of sulphuric acid or total sulphur in the ash. You will see that I found in one instance 4.88 per cent in the ash and 8.09 per cent in the plant, almost 66 per cent more.

Mr. Charles P. Beistle wrote as follows:

I would say that I have done considerable work on the determination of sulphur in plant substances and proteid bodies, and have found the only satisfactory way is by fusion in a mixture of sodium hydrate and potassium nitrate. Among other methods used were ignition in a closed vessel containing oxygen under about 20 atmospheres pressure, ignition in a combustion tube in a current of oxygen gas, passing products of combustion through bromin water, and digestion in nitro-hydrochloric acid. The first-mentioned method always gave the highest results. The next two methods gave almost as high results, but required special apparatus and a great expenditure of time. To determine sulphur in the ash of plants gives no indication whatever of the amount of sulphur present in the original material, and the calcium-acetate method (simple ignition with calcium acetate), although giving higher results, is of no real value as a method of estimating total sulphur.

I would suggest that fusion with sodium peroxid might be successfully used as a method of oxidizing the plant material and changing sulphur to sulphate.

Work on Ash.

Two samples were prepared, corn bran and cotton-seed meal, and sent out with the following letter:

DIRECTIONS FOR WORK.

The samples consist of corn bran and cotton-seed meal. Determine moisture (in the usual way), sulphur, and potash in both samples. Make at least two determinations by each method. In reporting give weights of precipitates, per cent on samples as received, and on dry matter. Please report results as early as possible.

Method I.—Sulphur.

Place 5 grams material in a 2½-inch porcelain evaporating dish, add 20 cc concentrated nitric acid, and heat the mixture cautiously on the water bath until all danger of overflowing has passed. Then evaporate partly, add 10 cc of 5 per cent solution of potassium nitrate, evaporate to complete dryness, and ignite, at first gently, then more vigorously until the residue is white. The residue is then dissolved in hydrochloric acid, evaporated to dryness, and heated for some time in an air bath to render silica insoluble. The residue is taken up in water with the addition of a little hydrochloric acid, filtered to 150 cc or more, and the sulphuric acid precipitated with barium chlorid in the usual way. Make a blank test with the reagents.

Method II.—Sulphur.

The same as the preceding, substituting 20 cc of a solution of calcium acetate for the potassium nitrate. The solution is prepared by dissolving 12.5 grams calcium carbonate, chemically pure, in chemically pure acetic acid, and diluting to 250 cc. Make a blank test with the reagents.

Method III.—Potash.

Determine by ignition with sulphuric acid as in the methods of the A. O. A. C., page 22 b. With the bran use a quantity of the solution corresponding to at least 2 grams of bran.

Method IV.—Potash.

Char 10 grams substance in a platinum dish, extract twice with hot dilute hydrochloric acid 1:10, and wash, receiving the extract and washing in a 500 cc flask. Return filter and contents to the dish, and ignite to whiteness. Dissolve the residue in hydrochloric acid, add to the extract in the flask, make up to volume, and determine potash as in Method III.

Report potash as K_2O, sulphur as SO_3. Please give the referee the benefit of your suggestions in regard to the work.

MOISTURE.

The moisture determinations on the samples sent out are given simply as a matter of record (Table III). The agreement is satisfactory.

Table III.—*Moisture determinations.*

Analyst.	Corn bran.	Cotton-seed meal.
	Per cent.	*Per cent.*
J. H. Gibboney, Virginia	12.10	7.28
E. G. Runyan, Washington, D. C.	12.67	7.20
Frank T. Shutt, Ottawa	12.30	6.97
A. T. Charron, Ottawa	12.55	7.08
R. W. Thatcher, Washington	13.02	7.96
	13.07	8.01

DETERMINATION OF SULPHUR.

The results obtained for sulphur in the samples as sent out are given in the following table:

TABLE IV.—*Determination of sulphur (SO_3).*

Analyst.	Corn bran.		Cotton-seed meal.	
	Provisional method.	Modified provisional method.	Provisional method.	Modified provisional method.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
J. H. Gibboney, Virginia	0.27	0.32	1.06	1.07
	.28	.34	1.07	1.10
	.28	.30	1.01	1.00
E. G. Runyan, Washington, D. C.	.43	.33	1.04	1.08
	.42	.34	1.05	1.08
	.44	.32	1.04	1.14
Frank T. Shutt, Ottawa	.40	.15	1.27	1.10
	.40	.13	.....	1.05
A. T. Charron, Ottawa	.34	.24	1.24	1.00
	.34	.24	1.34	1.08
G. S. Fraps, North Carolina	.....	.41	.....	1.03
	.....	.40	.....	1.00
	.....	.....	.....	1.03
	.....	.....	.....	1.08
R. W. Thatcher, Washington	.27	.24	.99	.97
	.23	.25	1.00	.97

REMARKS OF ANALYSTS.

R. J. Davidson, Virginia.—We tried several determinations on these substances by Eschka's method, but found the result too low. On 2-gram samples we got the following weights of barium sulphate: 0.0240, 0.216, and 0.0209 grams, just about one-third of what they should be.

R. W. Thatcher, Washington.—My experience with the two methods suggested for the determination of sulphur is that they give practically identical results, those obtained by the calcium acetate ignition method being very slightly lower. The use of calcium acetate allows much more rapid burning to whiteness, since the potassium nitrate present in the other method fuses very easily, and thus incloses particles of carbonaceous matter, which are finally removed only after a somewhat tedious process.

Frank T. Shutt, Central Experimental Farm, Ottawa, Canada.—We found great difficulty in obtaining a white ash by Method II. Even after prolonged ignition the ash remained gray, and on treatment with acid showed the presence of carbon. You will notice that invariably higher results were obtained by Method I. As far as one can judge from duplicate determinations and general conduct and appearance of the material during treatment, Method I seems to be very satisfactory. To lessen the danger from loss while frothing (treatment with nitric acid on water bath) a 3-inch porcelain evaporating dish was used. It will be found much safer than a 2½-inch dish. Ignition in a muffle furnace proved easier and quicker than with the blast lamp.

The agreement between the figures obtained by different analysts by both methods is not satisfactory. The trouble is with the methods. They are not very accurate. As will be shown below, the results given by the nitric acid method are much lower than they should be.

WORK OF H. C. SHERMAN ON SULPHUR AND PHOSPHORUS.

H. C. Sherman, of Columbia University, New York City, during the past summer has been studying the methods for the determination of sulphur and phosphorus in organic materials. We have had some correspondence on the subject, and he has kindly communicated to me the results of his work, which will appear in the Journal of the American Chemical Society. The methods which Dr. Sherman has studied are as follows:

(1) Combustion in oxygen under pressure of 25 to 30 atmospheres in the bomb calorimeter.

(2) Fusion with alkali, as described by Osborne.

(3) The provisional method of this association (the nitric acid method), with the use of 2 grams of sample.

Six samples of material were used. In every case the nitric acid method gave lower results than the other two methods, the average amount of sulphur found being about five-sixths of that present. It seems probable that the greater part of the discrepancy is due to volatilization of sulphur in some form of combination not sufficiently oxidized to stand the heat generated at this point. Such a loss could doubtless be avoided by repeated evaporation with nitric acid, or by the addition of alkali along with the nitrate, but the method would thus become practically that of Salkowski. Combustion in oxygen has the advantage over the fusion method.

The fusion method is described by Osborne as follows: [a]

About 10 grams of sodium peroxid were converted into hydroxid in a nickel crucible by adding a little water and boiling over an alcohol lamp until the excess of water was expelled. From 1 to 2 grams of the protein were then stirred into the slightly cooled hydroxid and oxidized by gradually raising the heat and adding small portions of sodium peroxid until the oxidation was complete. The fused mass was then dissolved in 400 cc of water, its solution strongly acidified with hydrochloric acid, boiled until the excess of peroxid was destroyed and chlorin expelled, filtered, made neutral with ammonia, and an excess of 4 cc of concentrated hydrochloric acid added. From the boiling solution sulphuric acid was precipitated by gradually adding a solution containing 1 gram of barium chlorid. After standing overnight on a steam table the barium sulphate was filtered out, washed, ignited, and weighed.

Dr. Sherman uses 15 grams of sodium peroxid, and with vegetable materials the acidulated solution was evaporated to dryness, and heated, to dehydrate any silica which might have been present.

This method differs from that tested by the referee chiefly in the use of a larger volume of water in the solution from which the barium sulphate was precipitated. As it is well known that barium sulphate is soluble in strong solutions of salts, it is possible that this may account for the difference.

Dr. Sherman exchanged samples with the referee, with the following results. The sample of lean meat was sent by Dr. Sherman. The other two samples are the referee's samples.

TABLE V.—*Comparison of methods for the determination of sulphur.*

Method and analyst.	Lean meat.	Cotton-seed meal.	Corn bran.
	Per cent S.	*Per cent SO_3.*	*Per cent SO_3.*
Compressed oxygen method—Sherman	0.82	1.49	0.47
Fusion method—Sherman	.81	.....	.....
Nitric acid method—Sherman	.68	.....	.....
Nitric acid method—Fraps	.57	1.03	.40
	.52	1.07	.41

[a] Jour. Am. Chem. Soc. 24: 142 (1902).

I am convinced by this work that the nitric acid method gives too low results.

Determination of Potash.

The results obtained by the different analysts for potash by the methods already described are as follows:

Table VI.—*Potash determinations.*

Analyst.	Corn bran.		Cotton-seed meal.	
	Method I—Sulphuric acid.	Method II—Charring and extracting.	Method I—Sulphuric acid.	Method II—Charring and extracting.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
J. H. Gibboney	0.43	0.39	1.80	1.82
	.42	.39	1.78	1.82
E. G. Runyan	.37	.38	1.61	1.73
	.38	.36	1.56	1.68
	.....	.....	1.60	1.72
	.....	.....	1.64	1.77
R. W. Thatcher	.42	.37	1.74	1.64
	.45	.38	.....	1.72

There seems to be a slightly larger quantity of potash obtained by charring and extracting than by ignition with sulphuric acid, though the results are not conclusive.

Determination of Sulphates.

It has been suggested to the referee that not the total sulphur but the sulphur existing as sulphates in plants should be considered as the sulphur of the ash, since the organic sulphur would otherwise be counted twice. It is necessary, however, that we should have a method for the determination of total sulphur, in order to estimate the quantity of that element required by the growing plant; the fact should not be lost sight of for an instant that the determination of sulphur in an ash, as heretofore made, throws no light whatever upon the quantity of sulphur in the plant, and, since it leads to false conclusions, is worse than valueless.

That part of the sulphur in plants exists as sulphates, and part in the organic form, has been known for a long time. R. Arendt, in 1856, was the first to distinguish between organic and inorganic sulphur in plants and to estimate total sulphur with any degree of accuracy. He extracted the sulphates with acidulated water, and estimated the total sulphur by fusion with alkalies. Ulricht pursued a similar plan. Arendt (1857) found small amounts (0.04–0.06 per cent) of sulphates in the lower leaves and ears of the oats, and more in the upper leaves (0.22–0.44 per cent). Ulricht (1859) states that sulphates are totally absent from the lower leaves and stems of red clover, while present in the upper leaves and the blossom.

Wolff and his associates (1859) give the following quantity of sulphates and organic sulphur as present in the dry matter of green rape.

Table VII.—*Distribution of sulphur in green rape (Wolff).*

Part of plant.	Organic sulphur.	Sulphates.
	Per cent S.	*Per cent SO_3.*
Seeds	1.127	0.020
Straw	.167	.021
Chaff	.310	1.464

Wolff and Yelin (1860) did not find any sulphates in the grain or straw of wheat, in barley, oats, or lucerne. Knop and Ritter (1859) found sulphates in garden beans (0.14 per cent) but none in the bean straw.

E. Schulze [a] investigated the changes in sulphur during the sprouting of the seeds of the yellow lupine. The finely ground material was completely extracted with warm water, acidified with hydrochloric acid after separating a small quantity of albumen, and precipitated with barium chlorid. As the precipitate did not appear pure it was fused with sodium carbonate with the addition of a little potassium nitrate, the melt extracted with water, and the sulphuric acid precipitated with barium chlorid. The seed contained 1.028 per cent sulphur, 0.154 per cent as sulphates (0.385 per cent calculated as SO_3). The sprouted seeds contained 1.510 per cent and 1.703 per cent sulphur as sulphates after 12 and 15 days, respectively. An oxidation of organic sulphur took place during the germination.

Tammann [b] obtained 0.359 per cent SO_3 from peas, by fusion with sodium carbonate and saltpeter, and 0.075 per cent SO_3 precipitated by barium hydroxid from the hot water extract purified with tannic acid. After germinating 25 days, 0.191 per cent SO_3 was present—a decided increase. By boiling the alkaline filtrate from the barium sulphate with hydrochloric acid a second precipitate appeared, due, he says, to the presence of ethereal salts of sulphuric acid. The quantity of this second precipitate from the ungerminated seeds was insignificant as well as from the seeds germinated in darkness, while from those germinated in the light it corresponded to 0.019 per cent SO_3.

Berthelot and Andre [c] investigated the sulphur in different forms in plants at different stages of growth. They concluded that the sulphur content of the plant increases continuously until it blossoms. The amount of sulphur present in organic compounds reaches its maximum at the time of flowering, and then gradually decreases partly on account of reoxidation of the sulphur, partly by elimination of volatile sulphur compounds. The proportion of the two forms of sulphur in the seeds varies considerably in different species of plants. In *Avena sativa* nearly all the sulphur is present in the organic form; on the other hand, in the white lupine only 6.7 per cent of the total sulphur is in organic combination.

I have gone thus fully into the literature in order to give a clear idea as to the present standing of the determination of sulphates in plants. It is seen that the quantity of sulphates present may vary considerably, both in the seeds of different plants, different parts of different plants, different parts of the same plants, and in the same plant at different stages of growth. At times, indeed, the amount of sulphur present as sulphates is very small.

The following method was used for the determination of sulphates in several materials:

Five grams substance was mixed well with 50 cc of a 1 per cent solution of hydrochloric acid, allowed to stand half an hour, filtered, and washed with the dilute acid to 250 cc or more. The liquid was heated to boiling, barium chlorid was added, and the determination completed in the usual way.

Instead of the 1 per cent hydrochloric acid, water was used in several cases, but it was found to dissolve organic matter which was afterwards precipitated on coming in contact with the acid.

No sulphur as sulphates was found in the following materials: Corn, peas, green millet, timothy hay, corn silage, peanuts.

Sulphur as sulphates was found in the following: Oats (trace), crimson clover straw, 0.003 per cent; cotton-seed meal, 0.001 per cent; green cowpea vines, 0.085 per cent.

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[a] Landw. Versuchs. Stat. **19**: 172 (1876).

[b] Ber. d. chem. Ges. **19**: 261 (1886) Ref.

[c] Biedermann's Central-Blatt, 555 (1891).

Determination of Chlorin.

The writer has already called attention to the fact that chlorin as well as sulphur will be lost in burning a plant substance to an ash by itself. It will appear later that the loss is due to decomposition of the chlorids by the heated organic matter.

Chlorin was determined in a number of substances in two ways, namely, in the ash as prepared in the usual way and by fusion of the plant material with sodium hydroxid, a method which will be described in full later on in this paper. The results of the determination are as follows:

Table VIII.—*Chlorin in plants.*

Material.	Ash method.	Sodium hydroxid method.
	Per cent.	*Per cent.*
Corn	Trace.	0.040
Peas	.005	.008
Peas, No. 2	.001	.012
Oats	.005	.097
Oats, No. 2	.001	.056
Peanuts	.008	.017
Cotton-seed meal	.008	.032
Cotton-seed hulls	.005	.013
Linseed meal	.010	.029
Millet	.120	.187
Corn silage (dry)	.310	.607
Green rape (dry)	1.261	1.290
Green peas (dry)	.160	.205
Sweet potatoes (dry)	.341	.362
Timothy hay	.864	.888

It is evident that a considerable proportion of the chlorin in plants may be lost in burning them to an ash, particularly when there is only a small quantity of chlorin in the plant.

The cause of the loss is shown by the work of Davies, reported in the Journal of the Society of Chemical Industry.[a] He experienced similar losses when sugar, starch, or filter paper was ignited with sodium chlorid. The alkalinity of the ash was evidence that no base had been lost, and if the sodium chlorid was added after the sugar had been charred, and the ignition then completed, no loss took place; that is to say, the loss took place during the initial stages of the combustion, and not during the time the carbon was being burned off, and was probably due to the decomposition of the chlorids by the hot vapors from the organic matters. Extracting the material with hot water after charring and then completing the combustion can, therefore, have no effect on the loss of chlorin, since it takes place before the extraction. When sodium carbonate equivalent to 5 per cent of the organic matter was added to the material, the loss of chlorin was prevented.

Three methods for the determination of chlorin in plants were tested.

(1) *Ignition of the material with calcium acetate.*

Five grams substance were moistened with 20 cc of a solution of calcium acetate containing 0.56 gram calcium oxid, evaporated to dryness, and ignited. The ash was dissolved in nitric acid, filtered, and chlorin determined in the filtrate by the Volhard method. On account of the very small quantity of chlorin present in many of the substances, a gravimetric method could not be used as the precipitate would not coagulate. The results by this method are low (Table IX).

[a] Jour. Soc. Chem. Ind., **20**: 98 (1901).

(2) *Fusion with sodium hydroxid.*

Five grams substance were mixed thoroughly with 10 cc of a solution of 100 grams caustic soda in 200 cc water, evaporated to dryness, and finally fused. A nickel crucible was used for a portion of the work and silver crucibles for the remainder, due care being taken to prevent silver from being detached from the crucible. It is better to use nickel crucibles, as there is always a little danger of small particles of silver being detached. The melt was dissolved in water, neutralized with nitric acid, filtered, and chlorin determined in the filtrate by the Volhard method.

The method yields satisfactory results, but it is long, and the crucibles wear out rapidly.

(3) *Ignition with sodium carbonate.*

Five grams substance in a platinum dish are impregnated with 20 cc of a 5 per cent solution of sodium carbonate, evaporated to dryness, and ignited as thoroughly as possible. The residue is extracted with hot water, filtered, and washed. It is returned to the platinum dish, ignited to an ash, dissolved in nitric acid, and the chlorin determined by the Volhard method.

In one or two cases the filtrate from the first extraction was yellow from organic matter. It was returned to the dish with the charred residue, evaporated to dryness, and ignited. The residue burned very readily to a white ash. The sodium carbonate method gives as accurate results as the method of fusion with caustic soda, and as it is shorter and easier, it is to be recommended for use.

The results by the three methods are contained in the following table:

TABLE IX.—*Methods for chlorin.*

Material.	Ignition with calcium acetate.	Fusion with caustic soda.	Ignition with sodium carbonate.
	Per cent.	*Per cent.*	*Per cent.*
Corn	0.002	0.040	0.027
	.....	.040	.026
Millet	.148	.165	.188
	.....	.171	.194
	.....	.204	.....
Corn silage	.400	.616	.610
	.....	.599	.....
Cotton-seed meal	.031	.032	.020
Cotton-seed hulls	.010	.013	.017
Green peas	.215	.197	.228
	.....	.212	.239
Oats	.034	.056	.....
Timothy hay	.870	.914	.897
	.....	.878	.911
	.....	.872	.....

RECOMMENDATIONS.

The referee makes the following recommendations:

(1) Either that the method of fusion with sodium hydroxid and sodium peroxid be adopted as a provisional method by this association, or else that the referee on ash be requested to make a further study of the fusion method.

(2) That the method of determining chlorin by ignition with sodium carbonate be adopted as a provisional method.

The PRESIDENT. Next in order will be the report on potash. We will now listen to that report.

REPORT ON POTASH.

By H. B. McDonnell, *Referee.*

The work on potash was not taken up until after the appearance of the proceedings of the association for last year, and the work was necessarily planned rather hurriedly and without the careful preliminary work that is desirable.

Early in August a circular letter was sent out inviting cooperation in the work, and favorable replies were received from 12 laboratories, with requests for samples. Reports have been received from 9 laboratories, so that, including that of the referee, 10 laboratories are represented in the work, and 14 chemists.

It was recommended at the meeting last year (1) that the causes of low results obtained by the official method be investigated, (2) that the milk-of-lime method be submitted for investigation for the ensuing year, and (3) that our method of determining moisture in potash salts be compared with the German method.

The following directions were sent out with the samples:

Directions for the A. O. A. C. Potash Work, 1902.

The bottles sent, with samples to be prepared therefrom, are as follows:

Bottle 1, K_2SO_4, chemically pure; bottle 2, kainit; bottle A, acid phosphate; bottle B, blood; bottle C, fish.

Sample 1, K_2SO_4, chemically pure.

Sample 2, kainit.

Sample 3 { 10 per cent No. 1.
90 per cent A.

Sample 4 { 25 per cent No. 2.
75 per cent A.

Sample 5 { 10 per cent No. 1.
50 per cent A.
20 per cent B.
20 per cent C.

Sample 6 { 25 per cent No. 2.
40 per cent A.
20 per cent B.
15 per cent C.

Compare flasks with pipette before use.

Ingredients to be weighed separately into graduated flasks. Total charge, 10 grams for 500-cc flasks and 5 grams for 250-cc flasks.

Note if 250-cc or 500-cc flasks are used. Use former size for first test, the latter for duplicate. Referee recommends the optional use of 250-cc flask and 5-gram charge.

Report result of blank test on $PtCl_4$ solution with number of cubic centimeters. Report cubic centimeters $PtCl_4$ used, and strength.

Test samples 1 and 2 by the official method.

Test samples 3, 4, 5, and 6 by Lindo-Gladding method.

Test samples 3, 4, 5, and 6 by milk-of-lime method, as used last year.

Test samples 3, 4, 5, and 6 by the following method: Boil with water as in the Lindo-Gladding method, add ammonia in slight excess, then $BaCl_2$ solution in slight excess, then ammonium carbonate solution in slight excess to precipitate excess of barium; cool, make up to volume, mix, filter a portion, using a dry filter, transfer 50 cc to a dish (may be of porcelain), evaporate to dryness, heat carefully on hot plate or in air bath (so that loss will not occur by decrepitation on ignition), ignite to dull redness over Bunsen burner, add about 25 cc of hot water, filter and wash into a dish, add excess of platinum solution, evaporate and treat as usual.

Determine moisture in 1 and 2 by official method.

Determine moisture in 1 and 2 by heating to dull redness.

The German method for concentrated salts is to heat 10 grams of the sample in a covered platinum crucible for about 10 minutes, with small flame to dark-red heat. In salts rich in $MgCl_2$ avoid decomposition and loss of chlorin by covering the substance with freshly ignited lime, or else the chlorin is determined before and after ignition, and correction is made for its loss, paying attention at the same time to the absorption of oxygen.

Referee will test A, B, and C for potash, and will determine moisture in 1 and 2, and also in a few samples of commercial potash salts, by heating in a combustion tube and absorbing the water in $CaCl_2$.

Please have results in by September 27, as the association will meet on October 2.

H. B. McDonnell, College Park, Md.,
Referee.

H. D. Haskins, Amherst, Mass.,
Associate Referee.

Results of Cooperative Work on Potash.

The results reported are given in detail in the following tables:

Table I.—*Results of determination of potash in samples.*

Analyst.	Official method.		Lindo-Gladding method with HCl.			
	Sample No. 1.	Sample No. 2.	Sample No. 3.	Sample No. 4.	Sample No. 5.	Sample No. 6.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
H. B. McDonnell, Maryland	53.98	12.22	.....	3.07	.....	.....
	54.25	12.12	.....	3.07	.....	.....
Mean	54.12	12.17	.....	.....	.....	.....
T. R. Gough, Maryland	54.55	11.96	.....	.....	.....	.....
	54.55	12.08	.....	.....	.....	.....
Mean	[a] 54.55	12.02	.....	.....	.....	.....
H. D. Haskins, Massachusetts	[a] 53.39	11.95	.....	.....	.....	.....
M. H. Pingree, Pennsylvania	54.00	12.20	.....	.....	.....	.....
	54.10	12.24	.....	.....	.....	.....
Mean	54.05	12.22	.....	.....	.....	.....
John S. Burd, U. S. Dept. Agr	53.94	12.04	.....	.....	.....	.....
	53.74	12.02	.....	.....	.....	.....
Mean	53.84	12.03	.....	.....	.....	.....
B. F. Robertson, South Carolina	54.08	12.14	.....	.....	.....	.....
M. G. Donk, Florida	53.90	11.70	.....	.....	.....	.....
	53.90	11.70	.....	.....	.....	.....
	53.92	11.66	.....	.....	.....	.....
	53.88	11.66	.....	.....	.....	.....
Mean	53.90	11.68	.....	.....	.....	.....
Geo. Roberts, Kentucky[c]	54.08	12.10	.....	.....	.....	.....
	54.00	12.08	.....	.....	.....	.....
Mean	54.04	12.09	.....	.....	.....	.....
F. B. Carpenter, Richmond, Va	54.05	12.08	5.02	2.90	.....	.....
Geo. A. Hanvey, Richmond, Va	54.05	11.98	5.12	2.94	5.30	3.06
C. Glaser, Baltimore, Md	[a] 53.13	[a] 12.67	.....	.....	.....	.....
G. W. Lehman, Baltimore, Md	[a b] 53.99	[a] 11.18	.....	.....	.....	.....
	[a b] 53.90	[a] 11.08	.....	.....	.....	.....
	[a] 52.88	.....	.....	.....	.....	.....
	[a] 53.04	.....	.....	.....	.....	.....
General average	54.02	12.04	.....	.....	.....	.....

[a] Omitted from general average. [b] Not washed with NH_4Cl. [c] Comments by A. M. Peter.

TABLE II.—*Results of determination of potash in samples.*

Analyst.	Lindo-Gladding method.						
	Sample No. 3.	Sample No. 4.	Sample No. 5.	Sample No. 6.	A.	B.	C.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
H. B. McDonnell, Maryland	5.01	2.86	5.25	2.97	0.06	0.25	0.69
	[a]5.05	[a]2.73	[a]5.19	[a]3.09	[a].08	[a].26	[a].67
Mean	5.03	2.80	5.22	3.03	.07	.26	.68
T. R. Gough, Maryland	5.32	3.16	5.79	3.28	.20	.21	.53
	5.38	3.21	5.72	3.27	.24	.21	.56
Mean	5.35	3.19	[b]5.76	3.28	.22	.21	.55
H. D. Haskins, Massachusetts	[b]4.78	2.72	4.98	2.74			
M. H. Pingree, Pennsylvania	5.06	3.05	[c]5.31	[d]3.05			
	5.08	2.99	[c]5.31	[d]3.00			
Mean	[e]5.07	3.02	[e]5.31	3.03			
John S. Burd, U. S. Dept. Agr.	5.08	2.83	5.15	3.04			
	[a]5.14	[a]2.93	[a]5.19	[a]3.05			
Mean	5.11	2.88	5.17	3.05			
B. F. Robertson, South Carolina	5.26	2.93	5.33	2.99			
M. G. Donk, Florida	5.01	2.73	5.24	2.93			
	5.06	2.76	5.27	2.95			
	5.02	2.60	5.27	3.01			
	4.99	2.54	5.28	3.03			
Mean	5.02	2.66	5.27	2.98			
Geo. Roberts, Kentucky[f]	5.03	2.90	5.22	3.07			
	5.04	2.75	5.26	3.05			
Mean	5.04	2.83	5.24	3.06			
F. B. Carpenter, Richmond, Va.	5.01	2.70					
G. A. Hanvey, Richmond, Va	5.09	2.77	5.17	2.97			
G. W. Lehman, Baltimore, Md	4.87	2.64	5.13	2.73			
	4.90	2.69	5 15	2.81			
	4.99						
	4.95						
Mean	4.93	2.67	5.14	2.77			
Average	5.09	2.83	5.20	2.99			
Theory	5.46	3.06	5.62	3.19			

[a] 250-cc flask.
[b] Omitted from average.
[c] Ignition with H_2SO_4 and solution in water, 5.49 and 5.47.
[d] Ignition with H_2SO_4 and solution in water, 3.25 and 3.09.
[e] Used analyst's acid phosphate.
[f] Comments by A. M. Peter.

TABLE III.—*Results of determination of potash in samples.*

Analyst.	$BaCl_2$–Am_2CO_3 method.				Milk-of-lime method.			
	Sample No. 3.	Sample No. 4.	Sample No. 5.	Sample No. 6.	Sample No. 3.	Sample No. 4.	Sample No. 5.	Sample No. 6.
	Per ct.	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*
H. B. McDonnell, Maryland	5.02	2.82	5.27	3.03	5.04	2.91	.....	.....
	[a] 5.12	[a] 2.82	[a] 5.31	[a] 3.13	[a] 5.03	[a] 2.93	.....	.....
Mean	5.07	2.82	5.27	3.08	5.04	2.92	.....	.....
T. R. Gough, Maryland	[a] 5.18	[a] 3.14	[a] 4.92	[a] 2.87	[a] 5.28	[a] 2.90	[a] 6.40	[a] 3.75
	[a] 4.83	[a] 2.77	4.97	2.75	5.24	2.88	6.21	3.63
	4.91	2.70	[a] 5.17	2.95	.....	.....	.....	.....
	.....	2.70	5.27	.....	.....	.....	.....	.....
Mean	4.97	2.82	5.08	2.85	5.26	2.89	6.31	3.69
H. D. Haskins, Massachusetts	4.98	2.86	5.27	2.95	4.77	2.73	5.99	3.65
M. H. Pingree, Pennsylvania	5.02	3.08	5.25	.....	4.97	2.99	5.22	3.15
	[a] 5.14	[a] 3.01	[a] 5.38	.....	[a] 5.03	[a] 2.96	[a] 5.20	[a] 3.02
Mean	[a] 5.08	[a] 3.05	[a] 5.32	[a] 3.09	[a] 5.00	[a] 2.98	[a] 5.21	[a] 3.09
John S. Burd, United States Department of Agriculture	4.97	2.76	5.39	2.77	.....	.....	.....	.....
	[a] 4.92	[a] 2.73	[a] 5.20	[a] 2.83	.....	.....	.....	.....
Mean	4.95	2.75	5.30	2.80	.....	.....	.....	.....
B. F. Robertson, South Carolina	5.28	3.04	5.31	3.01	5.33	3.01	.....	.....
M. G. Donk, Florida	5.11	2.71	5.22	2.96	4.88	2.72	[b] 5.48	[b] 3.02
	.....	.....	.....	.....	4.90	2.75	[b] 5.50	[b] 3.08
Mean	.....	.....	.....	.....	4.89	2.74	5.49	3.05
G. A. Hanvey, Richmond, Va.	4.93	2.84	5.08	3.06	5.06	2.95	.....	.....
Average	5.04	2.87	5.23	2.97	5.05	2.88	5.75	3.37
Theory	5.46	3.06	5.62	3.19	5.46	3.06	5.62	3.19

[a] 250-cc flask. [b] Organic matter destroyed before making solution.

TABLE IV.—*Moisture in potash salts.*

Analyst and method.	1.	2.	9806 (Md., com.), KCl.	9807 (Md., com.), K_2SO_4.	9818 (Md., com.), KCl.	9975 (Md.), kainit.	10275 (Md., com.), NaCl and KCl, 12 per cent K_2O.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
C. G. Church, Maryland: combustion tube and $CaCl_2$	0.05	12.84	1.91	0.81	3.15	11.65	3.28
	.05	12.64	1.70	.98	3.19	11.88	3.33
T. R. Gough, Maryland:							
100° C.	.01	1.71	.84	.32	1.80	1.40	2.73
	.00	1.74	.90	.31	1.85	1.43	2.68
130° C.	.00	5.60	1.60	.73	2.97	5.37	3.00
	.00	5.65	1.59	.73	2.95	5.26	3.08
Red heat	.09	13.20	1.61	1.10	3.35	11.81	3.35
	.09	13.15	1.65	1.10	3.20	11.90	3.33
M. G. Donk, Florida:							
Official	.00	4.24	.....	.....	.....	.....	.....
	.00	4.27	.....	.....	.....	.....	.....
Ignition	.07	14.68	.....	.....	.....	.....	.....

TABLE IV.—*Moisture in potash salts*—Continued.

Analyst and method.	1.	2.	9806 (Md., com.), KCl.	9807 (Md., com.), K_2SO_4.	9818 (Md., com.), KCl.	9975 (Md.), kainit.	10275 (Md., com.), NaCl and KCl, 12 per cent K_2O.
C. Glaser, Baltimore, Md.:	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
100° C.	0.03	2.63					
Ignition on hot plate	.09	12.17					
G.W. Lehman, Baltimore, Md.:							
130° C.	.00	7.37					
Dull red heat	.08	14.31					

COMMENTS OF ANALYSTS.

H. D. Haskins, Massachusetts.—Ten grams to 500 cc were used for the tests; for the duplicates 5 grams to 250 cc were used. In the last set of determinations, by the new or last method, duplicates were not run on account of there being an insufficient amount of the acid phosphate or bottle A.

M. H. Pingree, Pennsylvania.—The first results were obtained from solutions of 10 grams made up to 500 cc; the second represent solutions of 5 grams made up to 250 cc. The amount of acid phosphate sent by referee being too small to complete the work, a similar sample found to contain 0.10 per cent K_2O was substituted, as noted in Table III (foot-note *c*). The samples of kainit, fish scrap, and dried blood, represented by the number 2 and the letters C and B, were very coarse and gave me considerable difficulty in obtaining uniform samples.

John S. Burd, United States Department of Agriculture.—You will observe the absence of results by the "lime method," and I have to report lack of success with same, in that I was unable to dissolve the excessive quantities of lime salts by the use of the ammonium chlorid washing mixture. Moisture in No. 1, official method, 0.01 per cent; by German method, 0.10 per cent. Moisture in No. 2, by official method: The sample did not attain constant weight after thirty-six hours at 130° C.; I therefore give the losses as recorded at six-hour intervals for that period: 6.46, 7.08, 8, 8.15, and 8.28 per cent. Moisture in No. 2, German method (with lime), 12.48 per cent.

A. M. Peter, Kentucky.—I am opposed to reducing the amount to be weighed out for potash in mixed fertilizers. Ten grams is none too large, and the use of a small quantity would tend to introduce irregularities from irregular distribution of the potash salts in the samples, even when carefully prepared. I believe it would be better to increase the amount of water used in boiling up the sample. In the case of potash salts the quantity weighed out might be reduced and the amount of water remain the same. This is our usual practice in this laboratory, and Mr. Roberts has followed it in his work. Allow me to suggest also that the two series of experiments which you propose for testing the relative merits of the use of 500 and 250-cc flasks will give you no data upon the real point at issue. When you are dealing with pure salts, as in these experiments, it is immaterial whether you weigh out 10 grams and make up to 500, or 5 grams and make up to 250 cc, but in a mixture the larger quantity is more likely to give a true result.

M. G. Donk, Florida.—Ten-gram charges were used in each case, as the hygroscopic nature of the kainit would not allow weighing of less than 2.5 grams with accuracy. The ignited residue, after evaporation with sulphuric acid was, with samples 3, 4, and 6, not perfectly soluble in hot water acidified with HCl, but a minute

gelatinous residue had to be filtered off. The milk of lime method carried out according to directions on page 18(c) of last year's Proceedings[a] gave a pure K_2PtCl^9 precipitate with 3 and 4, but the dissolved organic matter in 5 and 6, on evaporation with platinum solution, left an impurity which no amount of washing would remove. The K_2PtCl_6 crystals also were colored deep brown by this same impurity. The results were so far out that I left them out of the table. Those in the table are results obtained by the method described on page 20 of last year's Proceedings.[a] In this case also, although the material was ignited to redness till all sulphuric acid had been volatilized, the same trouble was met with, though much less pronounced. The crystals in this case were apparently pure, only the mat of the Gooch being colored. After weighing the Gooch and precipitate, I dissolved the crystals with hot water and made a second weighing to correct for the organic matter present, but no increase in weight could be detected on account of the coloring matter.

F. B. Carpenter, Richmond, Va.—All of the results are considerably below what we would expect. With results marked "HCl" the Lindo-Gladding method was followed, with the exception that 5 cc of HCl was added to the solution before boiling. While the average of these results are a little higher than those obtained by other methods, there does not seem to be the difference that we usually have obtained in our previous experimental work with this modification. I trust some of the members of the association will be able to make some modification of the method now in use which will give theoretical percentages. As you will see, this is quite a serious question from the standpoint of the manufacturer.

G. W. Lehmann, Baltimore, Md.—On sample No. 1, when precipitate was washed with 95 per cent alcohol only, results were 53.99 and 53.90 per cent K_2O. When washed with 80 per cent alcohol and 25-cc portions of NH_4Cl solution, as in official method, results were 52.88 and 53.04 per cent. Determinations on No. 3 were made four times, because the figures found did not correspond with the calculations, and I am absolutely at a loss to account for the discrepancy.

C. G. Church, Maryland.—Moisture by combustion and absorption. In each case 10 grams of the sample were heated at a low red heat in a hard glass tube in an ordinary combustion furnace, and the moisture thus liberated, absorbed by passing it through a U tube containing $CaCl_2$. The tube was weighed before and after the combustion, and the difference calculated as moisture. The average time of combustion per sample was twenty-five minutes. Samples Nos. 2 and 9975 show such a large percentage that it was thought that some chlorin might have been absorbed. This was tested by passing dry chlorin through the $CaCl_2$ tube. In two experiments there was practically no increase in the weight of the tube. Three results were obtained on No. 2, but only two were concordant.

COMMENTS OF REFEREE.

The new method sent out, which is a modification of the alternate method, has been used by me occasionally for some years to check results by the Lindo-Gladding method, and has always given fairly concordant results. The ignition of the residue is free from the frying and sputtering that takes place in the latter method, which often causes us to fear that potash is lost in the fine spray of acid that is thrown up. The ignited residue is usually completely soluble, except where much organic matter is present.

The milk of lime method is rapid, till one comes to washing the final precipitate, where the large amount of lime, salts, etc. is troublesome. The method is, of course, not applicable to samples containing organic matter, like samples 5 and 6, or ammonium salts, unless such samples are first ignited, as has already been pointed out by

[a] U. S. Dept. Agr., Bureau of Chemistry, Bul. 67.

the originators of the method. This limited application of the method is a very serious objection to it, especially in States that require the potash to be soluble in water.

The results further emphasize the fact that our methods fail to recover all of the potash from mixed fertilizers, especially those containing acid phosphate. The close agreement among all the methods certainly proves that the loss is due either to the fact that some of the potash forms an insoluble compound with silica or other substance present, or that it is "occluded" in the precipitate of phosphates, etc. Further work should be directed to the matter of getting the potash in solution. The low results are certainly independent of the size of the flask in which the solution is made. The theory that has been advanced that the potash salts are more liable to run in streaks in a sample than are the other ingredients, making it necessary to weigh out a much larger sample for that determination, I believe to be erroneous. Any irregularity in the potash salt surely will affect the nitrogen and phosphoric acid in the same ratio that it does the potash. Our concordant results on nitrogen with 1-gram charges and phosphoric acid with 2-gram charges certainly is sufficient argument against such a theory.

A copy of the method of analyzing potash salts, as practiced by the German chemists, was kindly furnished by Mr. von Herff. Two salient features of the methods are the weighing out of a charge of such size that the final weight of the precipitate will show the percentage without calculation, and also the fact that they change the potash to the form of chlorid, by precipitating the sulphuric acid by barium chlorid, before adding the platinum solution.

To get the theoretical percentage of potash, as given in the tables, the averages of results on samples 1 and 2 were taken, to which was added the amount of potash derived from the other ingredients, as shown by the analyses of the referee. The average results of the different methods agree very closely, and, averaging all results, the average loss of potash in Nos. 3 and 4, in which 10 per cent of sulphate of potash was used, was 0.40 per cent, or a little over 7 per cent of the total amount present. The average loss in samples Nos. 4 and 6, containing 25 per cent of kainit, is 0.20 per cent, or slightly less than 7 per cent of the total amount present.

While the determination of moisture is of minor importance to the fertilizer inspector, the important one being the content of the valuable constituents, it is desirable that our methods in this respect give accurate results. Probably this may be attained in the case of salts, though it will certainly be a difficult problem in the case of mixtures of organic compounds with potash compounds like kainit. The combustion method, absorbing the water in calcium chlorid, is easy of application, and I think will give good results, but needs further trial.

For recovering waste platinum, I prefer to keep the precipitates and filtrates separate. The precipitates are treated with hot water and the asbestos separated by filtration, the filtrate being acidified with hydrochloric acid and a little pure granulated zinc added to effect the reduction.

The alcohol filtrate is concentrated by evaporation and treated in the same way. The ammonium chlorid filtrate, which is caught in another filter bottle, is thrown away, as the amount of platinum in it is very minute.

Recommendations.

The referee recommends:

(1) That further experiments be made for the purpose of determining a method that will dissolve all of the potash in mixed fertilizers.

(2) That further experiments be conducted with methods for determining moisture in potash salts.

(3) That the method of analysis shall give some latitude for the judgment of the analyst in regard to the amount of substance taken.

The PRESIDENT. You have heard the report on potash. It has been announced that one paper on this subject is to be presented, but as it is not ready at this time it will be presented later.

Mr. DONK. I wished to present a paper on this subject, but did not have time to write a formal report and include the calculations. I would like, however, to say a few words as to the probable cause of the low potash results obtained by our present methods with mixtures containing acid phosphate.

LOW POTASH RESULTS OBTAINED BY THE PRESENT METHOD WITH MIXTURES CONTAINING ACID PHOSPHATE.

By M. G. DONK.

Working on the comparison of methods for estimating potash in mixed fertilizers, carried out according to the instructions of the referee, Mr. McDonnell, it was not possible with any of the three methods compared to recover all the potash added in preparing the samples. This is in harmony with the results of last year's work, one of the objects of which was to see if it is possible with the Lindo-Gladding method to obtain from mixtures of acid phosphate and potash salts the theoretical amount of potash added. The potash work for 1900 also brought out the fact that the Lindo-Gladding method fails to recover all the potash in mixtures of potash and acid phosphates. In 1900 the loss was 3.92 and 4.95 per cent, respectively, with the two samples used, and in 1901 the loss was 6.86 per cent, while my results for this year's work are no better. Thinking that the loss was occasioned by the potash being carried down by the precipitate of interfering substances, I performed the following experiment:

Sample No. 1: Potassium sulphate, 0.1 gram, and acid phosphate, 0.9 gram.

Sample No. 2: Kainit, 0.25 gram, and acid phosphate, 0.75 gram. Added 30 cc of water and boiled for thirty minutes; filtered off the insoluble residue; washed and evaporated the filtrate down to 30 cc, when I removed lime, etc., by the Lindo-Gladding method. The precipitate I washed until free from chlorin and sulphate; dried at 100° C.; pulverized and again washed until free from sulphate and chlorin. Dissolved the precipitate with smallest possible quantity of hydrochloric acid, washed and diluted filtrate to 50 cc; then reprecipitated by addition of ammonia and a few drops of ammonium oxalate; filtered, washed, and determined potash in filtrate by Lindo-Gladding method. Sample No. 1 gave 0.029 per cent K_2O; sample No. 2, 0.071 per cent K_2O. The early meeting of the association prevented my experimenting along this line further, as was my intention, and a single test gives but meager data on which to base an opinion. Yet so far as it goes it tends to show that potash is occluded by the precipitate formed in the removal of interfering bodies in all the methods thus far tried. And this is to be expected from the nature of the process, for it is a well-known fact in chemistry that a chemically pure precipitate can but rarely be obtained from a solution containing other salts than the one it is desired to precipitate. Further, the more concentrated the solution the greater the contamination of the precipitate by the material in solution, and it is for this reason that I agree with Mr. Huston, who has found, as stated at the seventeenth annual meeting (see Proceedings, pp. 15 and 16), that the longer certain materials are heated the smaller the amount of potash found, owing to concentration of the potash solution from which the interfering substances must be precipitated. For the same reason a higher percentage is obtained by his method of passing steam through the solution instead of boiling, as no concentration is thus possible, while an increase in the volume of potash solution is brought about. This evil of the precipitate removing part

of the potash from the solution is inherent in every method thus far tried by the association. I was therefore much interested in a method first brought to my notice by Dr. Herzog, of Gainesville, Fla., in which it is possible to remove the potash from the solution in place of the interfering salts. This may be done by precipitating the potash as potassium phosphomolybdate in acid solution. The possibilities of this method have not been sufficiently tested to decide as to its accuracy, but it appears to me that by properly studying the conditions influencing the precipitation, as has been done for the optional volumetric method for phosphoric acid, it may be developed into a method by which it is possible to recover all the potash from such materials as make up the mixed fertilizers now on the market.

I wish to point out again the want of experimental evidence as to the statements first made, and would not have presented this paper but for the fact that it may suggest to others investigations along this line. In conclusion, I wish to say that if there are any members present who are in a position to offer any suggestions, information, or criticism on this proposed method I would be very glad for them to do so, as I am going to study it during the coming year.

The PRESIDENT. Is there anything to be said in response to this request?

Mr. CAVANAUGH. I may be able to answer the gentleman who has just spoken on the question of potash. The graduate school of our chemical department is working on that subject, and after one year reports very favorable results on the method last mentioned, carrying it on as a volumetric method. The results are agreeing better and giving more satisfaction than those obtained by the Lindo-Gladding method.

Mr. JAFFA. Mr. President, the committee to wait upon the Secretary and Assistant Secretary of Agriculture; and President Needham, of Columbian University, is ready to report, as follows: The president of the Columbian University said he would be glad to attend one of our sessions. We met the Secretary of Agriculture on our way, and he said he would be pleased to accept the invitation. The Assistant Secretary is out of town, but may return by Saturday morning. We will then call and extend the invitation.

Mr. DAVIDSON. I move that we adjourn until 1.30 p. m.

The motion prevailed, and the meeting adjourned at 12 o'clock noon.

THURSDAY—AFTERNOON SESSION.

The meeting was called to order at 1.30 p. m.

The PRESIDENT. The referee on foods and feeding stuffs has requested that he be allowed to defer his report until to-morrow morning. The next in order will be the report on dairy products.

Mr. CAVANAUGH. The report on dairy products will be a very short one. It will be only an attempt to throw a little light on the difficulties that have been experienced in the past.

REPORT ON DAIRY PRODUCTS.

By G. W. Cavanaugh, *Referee.*

In 1897 Dr. Van Slyke, as referee on dairy products, reported results on the determination of albumin in cow's milk. Three methods were tried. These same methods, with slight modifications, were again tried in 1898 and 1899. In 1900 and 1901 two more methods were added. The results of the coworkers have never been satisfactory. The following table shows highest and lowest results reported:

Table I.—*Determination of albumin in cow's milk.*

Method.	1897.		1898.		1899.		1900.		1901.	
	Minimum.	Maximum.	Minimum.	Maximum.	Minimum.	Maximum.	Minimum.	Maximum.	Minimum.	Maximum.
	Per ct.	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*
1	0.251	0.370	0.560	0.660	0.350	0.554	0.140	0.380	0.210	0.328
2	.175	.431	.390	.460	.460	.564	.100	.450	.240	.345
3	.373	.....	.440	.600	.....	.....	.310	.530	.270	.375
4	.....	.....	.....	.....	.....	.....	.350	.610	.210	.312
5	.....	.....	.....	.....	.....	.....	.020	.610	.280	.312

During these five years the samples of milk were preserved with formalin. Van Slyke mentions the proportion, 1 cc of a 40 per cent solution per liter. His report shows it to be a good preservative for milk when casein is to be determined, but no figures were given for albumin. No mention is made by the other referees of the amount of formalin used.

On page 114 of the Proceedings for 1901[a] I find the following resolution:

Resolved, That it is the sense of the association that until a proposed new method or modification of an existing method has been tested by the referee with favorable results it shall not be submitted by him for general test by this association.

Looking over the results of the last five years, the referee decided to try the methods before sending out samples. The present official method was first tested on a sample of fresh whole milk, and one of fresh separated milk. Samples for duplicate determinations were removed and then formalin was added to preserve the remainder. The following table shows the amounts of albumin found during a period of four days:

		Per cent.
First day	a. m	0.525
	p. m	.508
Second day	a. m	.463
	p. m	.376
Third day		.358
Fourth day		.157

Mr. B. B. Turner, Ph. D., using the official method on a fresh sample found 0.479 per cent and after three days, with the sample preserved with formalin, 0.122 per cent. These few figures are only a sample of the discouraging results obtained in the referee's laboratory, In looking for a possible explanation the following facts are observed: The existing official and provisional methods give satisfactory concordant results when tried on fresh milks. The same methods in the hands of chemists who have reported to the referees during the last five years give very unsatisfactory results. The milks were all preserved with formalin. In 1900 the lowest figure was reported from Oregon to the referee in New York. This agrees with the referee's figures given above.

[a] U. S. Dept. Agr., Bureau of Chemistry, Bul. 67.

In the Zeitschrift für Physiologische Chemie,[a] Dr. F. Blum calls attention to a new class of compounds of albumin in the following words:

A few drops of formalin added to a solution of egg albumin prevents the coagulation of the albumin by heat even after the solution is concentrated and the formalin driven off.

It needs, of course, demonstration that a similar effect is produced on the albumin of milk, before this offered explanation has much weight. To test this, four portions of milk of 10 cc were set aside for two days with respectively 2, 4, 6, and 8 drops of formalin. They were then diluted with 90 cc of water and the official method was carried out as for albumin. The portions having the smallest amounts of formalin showed a slight precipitation on boiling. No. 3 gave but a faint opalescence, while No. 4 remained perfectly clear even after forty-five minutes' boiling.

I recognize that the preservative was added in proportions greatly in excess of that necessary to preserve milk. As this preservative is known to prevent the coagulation of egg albumin, it seems quite probable that a like effect may occur with milk albumin. For this reason the referee did not send out samples to other laboratories.

The PRESIDENT. We will now listen to the paper on potash to be presented by Mr. Ross.

Mr. Ross. I shall give a brief synopsis of the paper submitted by Mr. Hare:

THE DETERMINATION OF POTASH IN FERTILIZERS BY SUBSTITUTING MILK OF LIME FOR AMMONIA AND AMMONIUM OXALATE AS THE PRECIPITANT.

By C. L. HARE.

The Lindo-Gladding method for the determination of potash in fertilizers possesses one particularly objectionable feature: The evaporation and ignition of an aliquot with sulphuric acid for the purpose of expelling ammonia salts and destroying dissolved organic matter is a tedious process and involves probable loss from sputtering during evaporation. A reliable modification which would exclude this feature would be highly desirable. At the sixteenth annual meeting of the Association of Official Agricultural Chemists Mr. Ross presented a method based upon the use of barium carbonate as a precipitant for phosphates, iron, alumina, etc. He later suggested milk of lime as the precipitant, and the writer, in 1901, reported results obtained by collaborators on official methods for potash determination. The method employed is as follows:

Weigh out 10 grams of the sample and boil with about 350 cc of water for thirty minutes; while hot add milk of lime till slightly alkaline. Cool, make up to 500 cc with water, and remove 50 cc, corresponding to 1 gram. Acidify with hydrochloric acid, add platinum solution, and evaporate to soft dryness over water bath. The residue is then washed with 80 per cent alcohol and ammonium chlorid "wash," as in the Lindo-Gladding method.

In the case of fertilizers containing organic matter, treat 10 grams of sample with dilute sulphuric acid (1–1), and incinerate; moisten ignited mass with dilute sulphuric acid (1–1), and heat to aid in removing from the dish; boil with 350 cc water and proceed as before. The milk of lime precipitates all lime except that present as sulphate, and the solubility of the sulphate being only 1 in 500, the aliquot of 50 cc will contain only 0.1 gram of that substance, an amount readily removed by the ammonium chlorid wash water and insufficient to cause material trouble either when solution is made with water direct or after incineration with sulphuric acid.

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[a] See vol. 22, p. 127.

The potassium platinic chlorid crystallizes well, and, after washing with alcohol, the salts of lime appear in light flakes which require never more than six washings with ammonium chlorid "wash" for complete removal.

The modification possesses several advantages over the Lindo-Gladding method: (1) The precipitation of lime is immediate, and there is no delay at this point; (2) evaporation to expel ammonia salts is eliminated; (3) probable loss of potash during evaporation is obviated; (4) washing the potassium platinic chlorid with alcohol and ammonium chlorid "wash" may be performed thoroughly with greater ease and rapidity, while no larger amount of platinum is required than by the Lindo-Gladding method.

The accuracy of the method is evidenced by results as shown in the tables. It has been used by the writer upon several hundred samples of miscellaneous fertilizers as a check against the Lindo-Gladding, and it is evident that the modification would not be applicable to fertilizers containing ammonia salts.

Table I gives parallel results by the milk-of-lime and the Lindo-Gladding methods upon fertilizers containing no organic materials, solution in each case being made by boiling the sample with water:

TABLE I.—*Determination of potash in fertilizers containing no organic materials.* [a]

Lime method.	Lindo-Gladding method.	Lime method.	Lindo-Gladding method.	Lime method.	Lindo-Gladding method.	Lime method.	Lindo-Gladding method.
Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
1.02	1.29	1.66	1.88	4.11	4.12	1.95	1.66
1.42	1.62	1.76	1.88	1.06	1.29	3.91	3.86
4.51	4.53	2.59	2.44	3.91	4.02	1.21	1.44
2.33	2.20	1.40	1.65	1.96	1.89	1.50	1.80
1.91	1.91	.84	.80	2.59	2.63	1.49	1.32
1.97	1.87	4.33	4.53	2.46	2.48	5.33	5.65
2.42	2.42	2.44	2.35	4.36	4.47	2.16	2.00
1.95	2.12	2.41	2.35	3.12	2.93	4.26	4.10
2.54	2.64	5.24	5.17	2.10	2.08	2.72	2.76
2.56	2.45	1.58	1.73	2.52	2.26	2.49	2.76
2.44	2.36	2.29	2.08	2.11	2.27	3.41	3.40
1.09	1.04	.81	.98	2.50	2.76	2.51	2.67
1.10	.90	2.37	2.29	4.37	4.33	4.21	4.04
2.14	1.89	3.66	3.90	2.49	2.74	2.77	2.41
1.75	1.89	2.44	2.88	1.75	1.89	2.04	1.88

[a] Solution by boiling sample with water.

Inspection of the tables reveals differences ranging from 0.01 to 0.27 per cent, with two exceptions, in a total of 60 samples. Of this number, 46 show differences less than 0.20 per cent, while the average difference is 0.10 per cent.

This average difference is, of course, without value as an indication of accuracy, unless considered in connection with the variation of each parallel determination, but when so large a percentage of duplicates falls within the limits of probable error the average in differences of the entire number of determinations indicates in a measure the comparative accuracy of the two methods.

Considering that the figures in the tables represent first results, and in no case a second determination by the same method, results by the milk-of-lime method appear quite as reliable as those obtained by the Lindo-Gladding method. In the regular course of laboratory work duplicate determinations by one and the same method may easily show less closely agreeing results.

Table No. II shows parallel results obtained from fertilizers containing organic

materials, the samples in each case being treated with dilute (1–1) sulphuric acid and incinerated before making solution in water:

TABLE II.—*Determination of potash in fertilizers containing organic materials.* [a]

Lime method.	Lindo-Gladding method.	Lime method.	Lindo-Gladding method.	Lime method.	Lindo-Gladding method.	Lime method.	Lindo-Gladding method.
Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
2.16	2.21	2.37	2.60	1.59	1.57	2.44	2.63
1.87	1.84	1.92	1.96	2.73	2.59	2.20	2.29
2.58	2.53	1.66	1.70	1.32	1.46	3.22	3.11
1.71	1.70	2.59	2.45	2.37	2.10	2.21	2.13
1.31	1.51	2.33	2.38	2.71	2.61	1.31	1.31
2.13	2.24	2.09	2.11	2.65	2.53	2.41	2.28
2.27	2.39	2.12	1.96	2.16	2.20	2.28	2.33
2.46	2.48	3.46	3.33	2.61	2.89	3.67	3.46
1.48	1.49	2.41	1.93	1.62	1.82	3.38	3.36
1.35	1.08	2.47	2.50	2.66	2.42	.74	.84
1.59	1.60	2.46	2.73	2.38	2.08	2.34	2.22
2.07	1.80	4.84	4.69	1.97	1.78	2.69	2.60
1.51	1.50	2.53	2.57	1.16	1.20	2.43	2.44
2.49	2.38						

[a] Samples treated with dilute sulphuric acid and incinerated prior to solution in water.

By reference to Table II we find variations ranging from 0.01 to 0.48 per cent in a total of 53 determinations. Forty-one of these give differences of 0.20 per cent or less, results averaging 0.06 per cent higher by the lime method than by the Lindo-Gladding.

Table III contains results from fertilizers containing organic materials. Samples were ignited with sulphuric acid (1–1) before obtaining solutions for the lime method, while for the Lindo-Gladding, solution was obtained by boiling the unignited sample with water.

TABLE III.—*Determination of potash in fertilizers containing organic materials.* [a]

Lime method.	Lindo-Gladding method.	Lime method.	Lindo-Gladding method.	Lime method.	Lindo-Gladding method.	Lime method.	Lindo-Gladding method.
Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
1.62	1.66	1.92	2.11	4.00	3.87	2.88	2.60
2.02	2.19	2.58	2.74	.50	.69	2.24	2.21
2.14	2.11	2.38	2.23	2.18	2.47	2.97	2.94
.88	.74	1.92	2.09	1.18	1.20	1.43	1.26
1.11	1.06	2.71	2.64	1.96	1.73	1.95	2.06
1.82	1.55	1.56	1.34	1.78	1.68	1.84	2.14
1.53	1.68	1.98	1.96	2.00	2.07	1.93	2.14
1.61	1.63	1.15	1,28	2.09	2.35	2.37	2.56
3.09	3.02	2.28	2.54	1.52	1.62	1.65	1.81
1.84	2.06	1.29	1.53	1.80	1.78	3.70	3.46
2.05	2.10	2.53	2.29	2.17	2.25	3.41	3.52
2.43	2.32	1.32	1.28	1.62	1.70	1.54	1.30
2.52	2.65	2.26	2.07	1.65	1.71	1.35	1.48
2.95	2.86	1.50	1.49	2.38	2.43	2.68	2.80
2.00	2.29	1.88	1.60	1.83	1.64	2.85	3.13
1.95	2.03	2.94	3.00	2.63	2.37	3.03	3.02

[a] Lime method: Samples ignited before solution. Lindo-Gladding method: Unignited sample boiled with water.

These results show an extreme variation of 0.29 per cent in a total of 63 determinations. Forty-six of the 63 vary less than 0.20 per cent, while the results average 0.02 per cent lower by the lime method.

In Table IV may be found results on fertilizers containing organic materials, solutions of both methods being obtained by boiling the sample with water. The solutions for the lime method were considerably colored by dissolved organic matter.

TABLE IV.—*Determination of potash in fertilizers containing organic materials.* [a]

Lime method.	Lindo-Gladding method.	Lime method.	Lindo-Gladding method.	Lime method.	Lindo-Gladding method.	Lime method.	Lindo-Gladding method.
Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
1.27	1.21	1.43	1.08	2.50	2.05	2.17	2.24
1.04	1.15	1.79	1.71	2.69	2.31	5.85	5.56
2.71	2.61	5.51	5.51	2.15	2.18	2.16	1.87
1.34	1.16	5.03	4.61	1.54	1.17	2.30	1.83
1.74	2.06	2.01	1.92	1.95	2.04	2.43	2.09
1.38	1.21	2.48	2.18	2.57	2.35	2.40	2.25
2.87	2.44	2.70	2.20	2.50	2.24	1.00	1.10
2.65	2.35	2.64	2.40	2.19	2.14	2.41	1.93
2.28	1.83	3.42	3.38	2.11	2.11	2.30	2.10
2.50	2.54	2.53	2.42	1.16	1.20	.....	.....
1.28	1.25	2.23	1.80	2.43	2.45	.....	.....
2.41	2.14	2.35	2.49	1.29	.99	.....	.....

[a] Samples boiled with water.

Although little was expected from the results obtained by the lime method under these conditions, still they show an extreme variation of only 0.55 per cent in a total of 45 determinations, while 30 of the 45 differ less than 0.30 per cent and the average difference is only 0.15 per cent. Nothing is claimed for the method when used under these conditions, but it is interesting to note that the method gives many good results, even when precipitation of platinum takes place in a solution considerably colored with organic matter.

Mr. CRAMPTON. Mr. President, I would like to say that if any member of the association knows of a test for the presence of palm oil in small quantities, less than 1 per cent, in mixtures of other fats (oleomargarine) and will communicate with me direct he will confer a great favor. Such a test is very much needed in the administration of the new internal-revenue law taxing artificially colored oleomargarine.

Mr. JAFFA. I would like to say that an invitation has been extended to Dr. Munroe to attend this meeting. He thanks the association for the invitation and will visit us to-morrow morning. I believe this completes our report.

Mr. DAVIDSON. Mr. President, I have been informed that the Census Bureau has published a bulletin entitled "Chemicals and Allied Products," prepared by Dr. Munroe, which would be of great interest to those who have not seen it. Dr. Munroe says that he, himself, can not furnish a sufficient number of copies to supply all the members of the association, and suggests that if the association should request copies for all the members they could probably be secured. I would

like to move that the secretary of this association be instructed to request Dr. Munroe to procure a sufficient number of copies of this bulletin to supply all the members with one.

Mr. McDonnell. I am quite sure, Mr. President, that all the members would be glad to secure a copy of this publication.

The motion prevailed.

The President. Has the referee on insecticides arrived?

Mr. Haywood. I have sent out for my report and it will be here in the next few minutes. I had not expected that it would come up this afternoon. In the meanwhile, I have a short communication here which was received from Mr. Gudeman, of Chicago, by Dr. Wiley, who asks me to read it. It is not on insecticides, but on feeding stuffs.

The President. If there is no objection, we will listen to the paper to be offered on feeding stuffs.

GLUTEN FEEDS: DETERMINATION OF FAT AND ACIDITY.

By Edward Gudeman, *Chicago, Ill.*

The extensive use of the maize gluten feeds, manufactured in starch and glucose factories, is a comparatively new thing. These feeds have been on the market about twenty years, but the present method of manufacture dates back only about five years. A large amount of work has been done and is being done on this class of feeds, especially by the agricultural experiment stations. The data published as to these feeds goes back to 1883 and comes up to 1900, and while mainly correct does not fully apply to the feeds as manufactured to-day. In many cases, as no distinction is made between the different feeds, the data is misleading.

The starch and glucose works of the United States have a daily capacity of about 225,000 bushels of corn. Of this quantity about 15 pounds per bushel is obtained in the form of cattle feeds. The yearly production is about 500,000 tons, 75 to 85 per cent of which is consumed in the United States, the remainder being exported. The exports are confined mainly to the gluten meal and the corn oil cake. The factories are located in the East and West, and depend on the whole corn belt for their raw material, about 68,000,000 bushels per year, which amounts to about 3 per cent of the average annual corn crop of the United States.

Corn varies in composition and it would be natural to expect these feeds to vary accordingly. This is not the case, and in a well regulated factory the feeds run very uniformly, much more so than wheat bran, cornmeal, or any of the common cattle feeds made from raw cereals. The kernel of corn is divided into its component parts, and while the proportions of these vary the parts themselves remain practically constant. As the process of manufacture of these feeds has a direct bearing on the analytical results, a brief superficial outline of the same is necessary.

Shelled corn is soaked in warm water thirty-six to sixty hours. This water contains a small amount of sulphurous acid and about 8 gallons of it is required per bushel. The corn swells and absorbs about one-half of this acid water. After soaking the required time, the sulphur water is drawn off, and as this contains a large amount of soluble substance of high feeding and fertilizing value, it is concentrated and mixed with the feeds in the same proportion as it is obtained from the corn. Analyses of the dry substances contained in this extract will show 6 to 10 per cent salts and 15 to 30 per cent of protein ($N \times 6\frac{1}{4}$). Sulphurous acid acts peculiarly on the kernel, penetrating strongly into the same and quickly loosening the intercellular tissue, thereby causing a good separation of the starch from the gluten at a later

stage of the process. It also acts as a preservative, preventing to some extent the fermentation of the grain.

The soft wet corn is very coarsely ground in such a way that the germ is separated without being broken, cut, or crushed. This mass is made up to a certain specific gravity with starch milk and placed in suitable tanks. The heavy material will sink to the bottom while the light oily germs float. These tanks are so arranged that this separation is a continuous and automatic one. The germs are washed free from all adhering starch, pressed and run into driers with about 50 per cent of water from which they are discharged with less than 3 per cent of water. The dry germs are now treated exactly as linseed; ground, cooked, steamed, and subjected to hydraulic pressure, giving the corn oil and the corn oil cake, the latter, if ground, being known as germ oil meal.

The mass that sinks to the bottom of these tanks is reground to a very fine pulp and thoroughly washed on bolting-cloth sieves. The starch and the gluten pass through the sieve and the coarse material (the bran) over the end of the sieve. This bran is pressed and goes to the driers with 50 to 60 per cent water, comes out of them with about 12 per cent, and is sold as corn bran or under some fancy name. To separate the germs and the bran from the starch and the gluten, about 60 gallons of fresh water are used per bushel of corn. All of this water is run into tanks for concentration and recovery of the starch and gluten. After concentration it is again diluted with about 60 gallons of fresh water per bushel of corn and run on the starch tables, where the starch deposits and the gluten flows off into another series of concentrating tanks, where it is allowed to settle before going to the presses. The pressed gluten goes to the driers with 50 to 60 per cent water and is dried down to about 12 per cent, which gives the gluten meal of commerce. A mixture of gluten meal and corn bran in the same proportion as obtained from the corn is the gluten feed of commerce. Generally this mixture is made wet before the bran or gluten has been pressed.

All the waters separated in these various tanks go directly to the sewer, carrying along all soluble impurities and the sulphurous acid absorbed by the corn in the soaking process. All in all about 120 to 130 gallons of fresh water are used to a bushel of corn to wash out the starch from the germ, bran, and gluten. As the feeds and germs contain about 50 per cent of water as they go into the driers and the same percentage is in the starch separated on the tables, we have 110 to 120 gallons of water per bushel that have been discharged into the sewer, and it is self-evident that very little of the acid used for soaking the corn will remain in the feeds. The small amount that is found in these feeds comes from the concentrated soak water that is added to the feeds after they have been pressed. The larger percentage of this is lost during the drying of the feeds. The concentration of this soak water in vacuum pans takes out fully 90 per cent of the sulphurous acid before the same is added to the feeds.

The old process, now almost completely discarded, made use of alkali to separate the starch from the gluten. This gluten had to be acidified before it could be economically handled. Sulphuric acid was commonly used, quite in excess, to make the gluten settle. This settled gluten was pressed or mixed with bran and then without any further washing went to the driers. Such feeds were high in acid, and there are records of cattle having become mouth-sore owing to the excessive amount of sulphuric acid in these feeds.

The methods of the Association of Official Agricultural Chemists are the standards used in the United States for making feed analyses. The methods for the determinations of water, ash, fiber, and crude protein ($N \times 6\frac{1}{4}$) give satisfactory results. The method for the determination of fat, applied to this class of feeds, is open to criticism. For the determination of acidity no official method exists, and none of the methods known to me give like results.

The official method for the fat determination says: "Extract the substance dried as for the determination of moisture." This means drying the substance in hydrogen or vacuum for five hours. As a general rule the drying is prolonged from eight to twenty-four hours. Drying the gluten feeds in hydrogen, vacuum, or air modifies the fat materially, besides changing the character of other constituents. The fat is made partly insoluble in ether or carbon-disulphid. The error due to this change in the solubility of the fat is often sufficient to class a feed below its guaranteed standard if the fat is just up to this standard.

TABLE I.—*Percentages of fat in gluten feeds.*

Samples and preparation.	Extracted with—	Forms of feed sampled.			
		Gluten meal.	Gluten feed.	Corn bran.	Germs.
Samples A:		*P. ct. fat.*	*P. ct. fat.*	*P. ct. fat.*	*P. ct. fat.*
Without drying	CS_2	4.74	3.02	3.97	.....
Dried over H_2SO_4	do	4.72	3.05	3.97	.....
Dried in hydrogen	do	3.60	2.61	3.74	.....
Dried in vacuum	do	3.62	2.61	3.75	.....
Dried in air	do	3.60	2.62	3.75	.....
Samples B:					
Dried in hydrogen	Ether	3.55	2.67	3.83	.....
Dried in hydrogen	CS_2	3.61	2.67	3.81	.....
Dried in air	do	3.58	2.68	3.80	.....
Not dried	Ether	4.68	3.00	3.93	.....
Not dried	CS_2	4.66	3.01	3.96	.....
Samples C:					
Not dried	Ether	5.16	6.19	5.32	.....
Not dried	CS_2	5.14	6.21	5.32	.....
Dried in hydrogen	do	3.56	4.97	4.73	.....
Dried in hydrogen	Ether	3.56	4.96	4.71	.....
Germ samples:					
Dried	do	.....	.....	.....	41.79
Not dried	do	.....	.....	.....	42.39
Wet germs	do	.....	.....	.....	44.93
Dried	CS_2	.....	.....	.....	41.85
Not dried	do	.....	.....	.....	42.39
Wet germs	do	.....	.....	.....	44.87

These results show very marked differences before and after drying. The greatest differences are found with the gluten meal, smaller ones with the gluten feed, still smaller with the bran, and very small variations with the germs. The physical condition of these products easily accounts for these results. The meal is in small balls and the first drying during the process of manufacture affects only the surface. The preparation of the sample for analysis, grinding so as to pass through a 1-mm sieve, exposes an immense amount of fresh surface to the direct action of the heat during the extra five to twenty-four hours' drying in the laboratory. The amount of fresh surface exposed with the other products is a great deal less, and therefore the differences in the extraction's results are less also. The extraction of samples of feed, grinding some before, and some after drying, shows differences of 0.1 to 0.3 per cent, the higher results being obtained on the samples that were dried in the coarse condition. The bran is in such a condition that a large surface is exposed in the original drying during manufacture and subsequent drying in the laboratory has very little further effect. The grinding of this product also exposes comparatively little new surface and the extraction figures, drying before and after grinding, do not differ materially. The gluten feed being a compound product of the other two, the results are between

those of the two component parts. The germs are in the course of manufacture very thoroughly dried to below 3 per cent, and the subsequent drying of same in the laboratory gives only slightly lower figures. The fat in germs that were dried over sulphuric acid or not at all, will be from 2 to 4 per cent above that found in the same sample after drying. Corn oil in a very finely divided condition, as it exists in these feeds, will be easily partially oxidized and saponified. No appreciable differences were found by drying the feeds in air, vacuum, or hydrogen.

The change in the fat, due to this drying, affects the acidity of the feed and especially the acidity of the extracted fat. These factors are often determined and used as the basis of an opinion as to the character of the feed and of the raw material from which the feed was made. The acidity of the fat from gluten feeds, extraction having been made after drying, is from 20 to 40 per cent determined as oleic acid. The acidity of fat extracted before drying will be from 5 to 15 per cent.

The fat from dry germ oil cake will show as high as 60 per cent acidity. This can be explained and no doubt is due to the high heat and steaming of the finely ground germs before being pressed. Some of the figures obtained from one of the experiment stations some time ago agree very closely with results obtained by myself.

TABLE II.—*Determinations of fat and acidity in gluten feeds.*

[Experiment station work.]

Sample.	Fat in feed.	Acidity of feed.	Acidity of fat.	Oleic acid in fat.
	Per cent.	*cc N/10 alkali.*	*cc N/10 alkali.*	*Per cent.*
A	3.16	2.8	1.05	46.8
B	2.48	4.85	.55	39.1
C	2.60	4.80	.90	48.8
D	3.43	.75	.85	35.0
E	3.78	7.10	.65	24.3

The highest percentage of acid, found in sample E, is accompanied by the lowest acidity in the extracted fat. Sample C contains a higher percentage of acidity in the extracted fat than was originally found in the feed. If the acidity of the feed is exactly neutralized, the fat extracted without drying will be neutral, while the fat extracted after drying will again show acidity. No doubt a saponification takes place, which will account both for the lower percentage of fat found and for the higher acidity of the same. The determination of the acidity of the feed is also of no value as an indication of the quality of the feed. All cereals give acid reactions. If the gluten feed or meal has been made by the old alkali process, the presence of sulphuric acid can be easily determined. In the new process, the acidity is due to acid salts and proteids, but not to free acid. The acidity determination can not be made directly on the feeds, as color, proteids, and starch products interfere with the action of the alkali and the indicators. Washing out the acid is a very tedious operation, especially as large quantities must be used to get average figures. The following method I have found to give very satisfactory results:

Weigh out 100 grams, place in a large beaker or flask with 1,000 cc of water; stir or agitate every now and then for one hour. Pour the whole mass on a double filter paper. Reject the first 100 cc of the filtrate. Take 200 cc for the determination, figuring 10 grams of substance to 100 cc of the filtrate. Unless the acidity is very low, use normal caustic alkali for the titration; $\frac{1}{10}$ cc will give a quick color reaction with the indicators used. One can not titrate to a permanent shade, as the substances held in solution react both on the alkali and on the indicators. The error due to the strength of the titrating solution is much reduced by the large amount of substance titrated,

20 grams per test. The indicators used play an important rôle in the amount of acidity found. The average of a large number of tests gave the following results:

	cc normal alkali.
Phenolphthalein	11.1
Rosolic acid	6.7
Congo red	5.6
Litmus	5.5
Cochineal	4.0
Methyl orange	Neutral to alkaline

I prefer, and use, rosolic acid. Phenolphthalein gives very high results. Gluten feeds contain the proteids of maize and these react on indicators similarly to the proteids of wheat described by Osborne, who states[a] that the proteids of wheat are "neutral to litmus, alkaline to lacmoid," and that "it required 19 cc of decinormal alkali to neutralize 100 cc, using phenolphthalein."

Tests made to determine whether the fermentation of the feeds before drying had any effect on the finished products gave the following results:

TABLE III.—*Effect of fermentation before drying on acidity of gluten feeds.*

Condition of feed.	Acidity, measured by normal alkali, as indicated by—	
	Phenolphthalein.	Rosolic acid.
Before drying:	*cc.*	*cc.*
Unfermented	7.3	7.2
Fermented	28.3	27.1
After drying:		
Unfermented	12.3	7.4
Fermented	12.5	7.5

This proves conclusively that the fermentation of the feed before drying does not affect the finished product at all, and that the determination of the total acidity of these feeds is not a criterion as to the condition of the feeds before drying. The statements that a high acidity of gluten feeds shows that they were made from fermented products are not borne out by facts. All corn feeds show a higher acidity after drying than before. The drying of these feeds increases the solubility of the proteids, and changes the starch into gums and dextrins, also soluble.

TABLE IV.—*Effect of drying on acidity of gluten feeds.*

Feed and condition.	Extract as percentage of dry substance.	Acidity, measured by normal alkali, as indicated by—	
		Phenolphthalein.	Rosolic acid.
Gluten meal:	*Per cent.*	*cc.*	*cc.*
Before drying	1.2	0.4	0.4
After drying	2.1	.6	.5
Gluten feed:			
Before drying	4.2	6.0	5.8
After drying	6.2	11.7	6.0
Corn bran:			
Before drying	6.7	11.5	11.6
After drying	11.3	21.3	12.0

[a] Am. Chem. Journal, July, 1900.

When the extract contains about 2 per cent of dry substance, the percentage of crude proteids will be about 4 per cent of the same. As the extract increases the proteids increase, and an extract containing 10 to 12 per cent of dry substance will show up to 35 per cent of proteids ($N \times 6\frac{1}{4}$). No definite ratio exists between the extract and its content of proteids. The results obtained in the determination of fat, acidity of fat, and acidity of feeds can not be used in direct comparison with results obtained on other cereal products. The quality of the feeds can not be determined from the acidity of the feed nor acidity of the extracted fat. All these results are materially affected by the treatment given the samples in the laboratory and in justice to the manufacturer, and so as not to mislead the consumer in comparing analyses of feeds the analyses should be made on the samples as received by the analyst, instead of modifying them to meet the requirements of any special or universal method of analysis.

REPORT ON FOOD ADULTERATION.

By W. D. Bigelow, *Referee.*

Since our meeting a year ago preliminary reports have been prepared giving methods for the examination of cereal products and tea and coffee. This leaves but one subject which has not already been covered by our methods, and the omission in that case has been due to the serious illness of the referee to whom the subject was assigned.

Considerable work has been done during the past year in putting to further test the methods which have been adopted provisionally for the examination of foods. The result has been the suggestion of certain changes which are relatively unimportant, and whose number is so great as to make it impracticable to discuss them in detail before the association. Owing to this fact, and also to the fact that there are very few here this morning who have given special attention to methods for the analysis of foods, or who are greatly interested in the detail of these methods, I shall pass over the suggestions of minor changes with the statement that they meet with the approval of myself and associates, and with the recommendation that they be incorporated in the provisional methods and printed in order that they may be available to the association.

So far our work has been conducted as individuals. A few years ago comparatively few of our members were interested in methods of this nature. Since then the work has been taken up in many laboratories that have always been represented in the association, and the chemists of food-control laboratories in various States and cities look to us to suggest methods for their use and cooperate with us in the preparation of those methods. I believe that we have made sufficient progress with these methods to make it practicable to carry on collaborative work between different laboratories in order to investigate and compare the methods we employ. From this time on, therefore, we can work with the methods for the examination of foods in very much the same way as we have with those for the examination of fertilizers, soils, and feeding stuffs.

It was only by individual effort that the methods could have been mapped out on the extensive scale which has been adopted, but systematic collaborative effort will be necessary to work out these methods in the detail that is desired. As previously stated, I do not think it would be wise to discuss before the whole association the changes which we recommend this year in the provisional methods. At the same time, following the collaborative work which we plan for the coming year, I believe that provision should be made at future meetings of the association for the detailed discussion of the methods for the examination of foods, and that hereafter the conservative attitude which the association has adopted with regard to other methods of analysis be extended also to food methods.

In closing I wish to express my appreciation for the able and earnest manner in which my associates have conducted their work.

The PRESIDENT. You have heard the referee's report on foods. Is there any discussion of the subject?

Mr. BIGELOW. Perhaps it is not related to this subject, but I have a suggestion to offer which I was requested to make by Dr. Wiley. He asks that as many members of the association as can find it convenient take dinner to-morrow evening at Cabin John Bridge. He did not say that we were to be there as his guests, but he would be glad to have as many go as possible. The accommodations are good, and it is a nice ride, which I am sure all of you would enjoy. All who can find it convenient to start from the Ebbitt House soon after 5 o'clock we shall be glad to have go, and if they will hand me their names, I will try to make some arrangements.

The PRESIDENT. If there is no other business to come before the meeting we will listen to the report of the referee on the determination of nitrogen.

REPORT ON THE DETERMINATION OF NITROGEN.

By F. W. MORSE, *Referee.*

The referee, in accordance with the vote of the association last year, undertook the comparison of methods for determining the availability of organic nitrogen. Two methods were recommended by the previous referee for trial, namely, the neutral permanganate method, as modified by Mr. Street, and the alkaline permanganate method, as modified by Mr. Jones. The former has been adopted by this association as a provisional method, while the latter has not been regarded with much favor by the majority of analysts who have tried it.

Since nearly all the principal nitrogenous fertilizer materials have been worked upon in the past by the different methods, the referee considered it the best policy this year to confine the work to two typical materials combined with superphosphate in approximately the proportion which might occur in a mixed fertilizer, in order to determine how closely results by different analysts would agree, and to make plainer any defect in the manipulation of the method.

The materials selected were dried blood and cotton-seed meal, because both are known to be highly available to plants, while the alkaline method has always failed to indicate the availability of cotton-seed meal, owing apparently to its carbonaceous matter. The blood was a part of a bag of blood meal for poultry and calves, and contained 13.1 per cent of nitrogen. The cotton-seed meal was a standard brand and contained 7.49 per cent of nitrogen.

Four lots of material were prepared containing approximately 3.5 to 4 per cent of nitrogen. The mixtures all contained superphosphate while the nitrogenous material was arranged as follows: No. 1, blood; No. 2, cotton-seed meal; No. 3, two-thirds nitrogen from blood, one-third nitrogen from cotton-seed meal; No. 4, one-third nitrogen from blood, two-thirds nitrogen from cotton-seed meal.

All the materials were sifted through the standard sieve, with circular holes 1 millimeter in diameter, and then each lot was thoroughly mixed. The blood was apparently coarse because a large part of it was crystalline rather than fibrous. Two of the analysts reground the samples containing it.

Twelve lots of samples were sent to as many different laboratories. Accompanying the samples were sent the following instructions:

Directions for Work on Nitrogen, 1902.

Please determine total nitrogen in each sample by either of the official methods. Last year the referee called attention to the fact that prolonged digestion with the sulphuric acid in the Kjeldahl method raised the amount of nitrogen. Please note the length of time used in each digestion throughout the comparison. Please determine available nitrogen by the neutral permanganate method adopted provisionally at the last convention, and by Jones's alkaline permanganate method, which has so far been regarded unfavorably. The latter method used in accordance with Mr. Jones's practice offers some advantages over the former in the matter of time. The methods are described as follows:

The neutral permanganate method.—Into a 400-cc Griffin beaker, low form, weigh an amount of sample containing, approximately, 0.075 gram of nitrogen (samples containing material that has been treated with acid should be washed on a 9-cm S. S. No. 595 filter to 200 cc and transferred, filter and all, to beaker); digest this with 125 cc of permanganate of potash solution (16 grams of pure $KMnO_4$ to 1,000 cc of water) in a steam or hot-water bath for thirty minutes. Have the beaker let down well into the steam or hot water and keep closed with a cover glass, stirring twice at intervals of ten minutes with a glass rod. At the expiration of the time remove from bath, add 100 cc of cold water and filter through a heavy 15-cm folded filter. Wash with cold water, small quantities at a time, till total filtrate amounts to 400 cc. Dry and determine nitrogen in residue by Kjeldahl method.

The alkaline permanganate method.—Weigh out an amount of sample containing, approximately, 0.045 gram of nitrogen, and transfer to a 600-cc distillation flask. After connecting with condenser to which the receiver containing standard acid has been attached, digest with 100 cc of alkaline permanganate solution (16 grams of potassium permanganate and 150 grams of sodium hydrate dissolved in 1,000 cc of water) for 30 minutes below the boiling point. Then boil slowly until the distillation is completed.

Since the samples all contain superphosphates, it will be necessary to wash them as directed for the neutral method. This is not necessary for the alkaline method, as it is intended to be used. Comparisons of washed and unwashed charges will be appreciated however.

The troublesome features of these methods seem to be filtration in the neutral and distillation in the alkaline method. Suggestions for hastening these steps will be of interest.

Results of Analyses.

The methods were copied from the report of last year.

Returns were received from nine laboratories and included the work of twelve analysts. The following tables give their results in full:

Table I.—*Total nitrogen.*

Analyst.	Sample No. 1.	Sample No. 2.	Sample No. 3.	Sample No. 4.	Remarks.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	
T. C. Trescot, Washington, D. C.	3.78	3.30	3.82	3.73	Digested 2 hours.
	3.75	3.34	3.85	3.73	
	3.98	3.59	3.95	3.87	Digested 3 hours.
	4.09	3.60	3.95	3.85	
Department of foods and feeding, Hatch Experiment Station, Massachusetts	4.16	3.58	4.01	3.84	
	4.16	.....	3.99	3.84	Digested 3 hours, Kjeldahl method.
	4.15	3.56	3.97	3.81	
	4.17	3.64	4.07	3.96	Digested 3 hours, Kjeldahl with sulphate of potash.
	4.14	.....	4.06	3.92	
	4.14	3.63	4.03	3.92	
F. B. Carpenter, Virginia	4.18	3.59	4.06	3.97	
S. H. Sheib, Virginia	4.19	3.55	4.07	3.94	

TABLE I.—*Total nitrogen*—Continued.

Analyst.	Sample No. 1.	Sample No. 2.	Sample No. 3.	Sample No. 4.	Remarks.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	
L. A. Hill, New Hampshire ...	3.90	3.54	3.75	3.67	
	3.98	.....	.....	3.78	Digested 3 to 4 hours.
	4.00	3.54	3.89	3.73	
W. W. Braman, New Hampshire.	3.98	3.45	3.88	3.84	
	4.03	3.48	3.94	3.86	
A. L. Sullivan, New Hampshire	4.05	3.33	3.92	3.64	Gas pressure lower than normal.
	4.06	3.33	3.89	3.72	
J. Bernard Robb, Maryland...	4.03	3.50	3.95	3.77	
	4.05	3.47	3.93	3.79	Digested 1 hour.
	4.08	3.51	3.96	3.82	
C. H. Jones, Vermont	4.32	3.69	4.04	4.04	
	4.35	3.69	4.04	3.97	Digested 2½ to 3 hours.
	4.32	3.76	4.11	3.97	
F. W. Woll and Geo. A. Olson, Wisconsin.	4.16	3.58	4.01	3.93	
	4.19	3.58	4.01	3.98	
	4.17	3.60	4.08	3.95	Digested from 1½ to 5 hours.
	4.14	3.57	4.07	3.95	
	.....	.....	4.09	.....	
W. H. Scherffins and A. M. Peter, Kentucky.	4.08	3.49	3.97	3.79	Digested 3 hours.
	4.07	3.53	3.88	3.86	
	4.13	3.54	3.95	3.86	Digested 5 hours.
	4.12	3.54	3.94	3.87	
W. R. Perkins, Mississippi.....	4.02	3.48	3.89	3.90	

TABLE II.—*Insoluble nitrogen—Neutral permanganate method.*

Analyst.	Sample No. 1.	Sample No. 2.	Sample No. 3.	Sample No. 4.	Remarks.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	
T. C. Trescot, Washington, D. C.	0.68	0.37	0.94	0.72	Washed.
	.80	.25	.86	.83	
	1.90	.46	.91	.60	Not washed.
	1.78	.25	.72	.81	
Department of foods and feeding, Hatch Experiment Station, Massachusetts.	1.85	.40	1.22	.93	
	1.78	.39	1.15	.83	
S. H. Sheib, Virginia	.65	.30	.56	.61	
L. A. Hill, New Hampshire....	.42	.31	.70	.84	Not washed.
	.46	.56	.78	.80	
	.53	.23	.49	.52	
	.61	.31	.50	.40	
W. W. Braman, New Hampshire.	.92	.56	.87	.77	
	.40	.36	.56	.52	
A. L. Sullivan, New Hampshire	1.01	.38	.67	.50	
	1.28	.41	.67	.52	
C. H. Jones, Vermont.....	1.29	.35	1.06	.87	
F. W. Woll and Geo. A. Olson, Wisconsin.	.34	1.17	1.04	1.52	
	.36	1.12	.99	1.55	
W. H. Scherffins and A. M. Peter, Kentucky.	.39	1.20	.97	1.51	
	1.26	.45	1.48	.97	
	1.47	.49	1.33	.76	
	1.26	.36	1.53	.83	
	1.34	.32	1.05	.91	
W. R. Perkins, Mississippi.....	.59	.41	.70	.71	
	.59	.41	.68	.64	

TABLE III.—*Soluble nitrogen—Alkaline permanganate method.*

Analyst.	Sample No. 1.	Sample No. 2.	Sample No. 3.	Sample No. 4.	Remarks.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	
T. C. Trescot, Washington, D. C.	2.46	1.57	1.99	1.68	
	2.32	1.51	2.10	1.82	
Department of foods and feeding, Hatch Experiment Station, Massachusetts.	2.38	1.30	1.83	1.55	
	.....	.....	.....	1.53	
	2.35	1.30	1.82	1.51	
L. A. Hill, New Hampshire	2.73	1.82	2.31	1.82	Distilled very low.
	2.80	1.96	2.38	2.13	
W. W. Braman, New Hampshire.	2.99	2.00	2.71	2.57	Do.
	2.98	1.93	2.80	2.49	
A. L. Sullivan, New Hampshire	2.90	2.44	2.41	2.26	Do.
	2.97	2.27	2.57	2.54	
J. Bernard Robb, Maryland....	2.83	1.85	2.40	2.27	
	2.88	1.84	2.46	2.17	
	2.75	1.78	2.31	2.19	
C. H. Jones, Vermont	2.67	1.50	2.16	1.86	
	2.64	1.53	2.09	1.90	
F, W. Woll and Geo. A. Olson, Wisconsin.	2.22	1.28	1.81	1.77	
	2.33	1.18	1.84	1.78	
	2.27	1.40	1.96	1.75	
	2.17	1.33	1.79	1.70	
W. H. Scherffins and A. M. Peter, Kentucky.	1.64	1.25	1.47	1.37	
	1.79	1.25	1.41	1.36	
	1.83	1.26	1.34	1.48	
W. R. Perkins, Mississippi	2.81	1.56	2.31	2.05	
	2.79	1.62	2.47	2.18	
	2.75	1.54	2.34	2.07	

TABLE IV.—*Availability of nitrogen in neutral permanganate.*

Analyst.	Sample No. 1.	Sample No. 2.	Sample No. 3.	Sample No. 4.	Remarks.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	
T.C.Trescot, Washington, D. C.	81.63	91.36	77.21	80.05	Washed until neutral.
	54.34	90.25	79.49	81.86	Unwashed.
Department of foods and feeding, Hatch Experiment Station, Massachusetts.	55.45	89.00	69.64	76.05	
	57.21	89.15	71.24	78.53	
S. H. Sheib, Virginia.....	84.49	93.52	86.24	81.97	
L. A. Hill, New Hampshire	88.97	87.57	80.62	77.68	Unwashed samples.
	85.75	92.38	86.85	87.94	Washed samples.
W. W. Braman, New Hampshire.	83.50	87,57	81.84	83.36	
A. L. Sullivan, New Hampshire	71.85	88.28	82.82	81.70	
C. H. Jones, Maryland	70.20	90.57	73.89	79.45	
F. W. Woll and Geo. A. Olson, Wisconsin.	91.36	67.31	75.30	61.26	
W. R. Perkins, Mississippi	85.32	88.31	82.26	82.69	

TABLE V.—*Availability of nitrogen in alkaline permanganate.*

Analyst.	Sample No. 1.	Sample No. 2.	Sample No. 3.	Sample No. 4.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
T. C. Trescot, Washington	59.30	42.89	51.64	45.53
Department of foods and feeding, Hatch Experiment Station, Massachusetts.	57.26	56.22	45.45	40.00
	.....	.....	.....	39.47
	56.68	36.04	45.30	39.00
L. A. Hill, New Hampshire	69.17	53.39	61.53	52.95
W. W. Braman, New Hampshire.	74.50	56.64	70.33	65.71
A. L. Sullivan, New Hampshire	72.34	70.57	63.84	65.21
J. Bernard Robb, Maryland	69.63	52.00	60.91	58.15
C. H. Jones, Vermont	61.31	40.88	52.34	47.12
F. W. Woll and Geo. A. Olson, Wisconsin.	54.19	36.31	45.43	44.30
W. R. Perkins, Mississippi	69.23	45.21	61.01	53.84

COMMENTS OF ANALYSTS.

Department of Foods and Feeding, Hatch Experiment Station.—Mechanical conditions were not uniform; a considerable portion of each sample was coarse. The substances should be reduced so as to pass a sieve of No. 2 perforated sheet metal (400 perforations to the square inch). This is especially true of mixtures containing highly nitrogenous foods; otherwise sampling for nitrogen determinations or availability, where only a small amount is employed, is very unsatisfactory, and concordant results are practically impossible except by chance.

In the determination of total nitrogen, by the plain Kjeldahl method, the reagents used in the digestion were one-half gram resublimated metallic mercury (B. and A.), 25 cc chemically pure sulphuric acid, specific gravity 1.84 (B. and A.); and, in the distillation, 200 cc distilled water, 25 cc potassium sulphid solution, 1–25 (Merck), 100 cc sodium hydrate solution, 1–2 ("Red heart"), one-half gram granulated zinc (30 mesh, B. and A.)

In the determination of total nitrogen by the plain Kjeldahl method plus sulphate, the reagents used were the same as in the plain Kjeldahl with the addition of 10–12 grams of crystallized potassium sulphate (B. and A.), to facilitate the digestion and to insure more perfect oxidation.

The results were as follows:

(1) More perfect oxidation; this is noticeable in every case where cotton-seed meal is present; the average increase in nitrogen for the samples is 0.056 per cent, 3.943 per cent, and 3.887 per cent.

(2) More rapid oxidation; the solutions cleared—i. e., bulk of organic matter was destroyed in twenty-one minutes (average) as against forty-one minutes in the plain Kjeldahl method.

(3) There is less reaction upon the addition of water in preparing for the distillation than in the case of the plain Kjeldahl method.

The mechanical condition prevented the obtaining of closely agreeing results in both methods.

The neutral permanganate solution was prepared from pure crystallized reagent (Merck). The plain Kjeldahl method plus sulphate was used for the determination of the nitrogen in the insoluble residue. Unevenness of the samples and variation in action of the solvents probably account for the poor parallels. The objectionable features in the manipulation of this method are chances of error from repeated transferring, etc., length of time required, and difficult filtration.

The alkaline permanganate solution was prepared from pure crystallized potassium permanganate (Merck) and stick sodium hydrate, purified by alcohol (Merck). The results are apparently low. This can be accounted for, partly at least, by errors in the method as sent out:

(1) A weak, incorrectly prepared solution. Sixteen grams of powdered crystallized potassium permanganate and 150 grams of sodium hydrate should be dissolved in water, and after cooling made up to 1,000 cc.

(2) Substances too coarse to receive the maximum effect of the solution.

(3) Digestion too short. The heating should be maintained for one hour without distilling over, but not necessarily below ebullition, and the flask should be shaken occasionally to wash down adhering particles. The distillation should be conducted as usual, simply using care not to break the flask. The objectionable feature in the manipulation is the adhering of the material to the sides of the flask and the smallness of the solution with which to wash it down. Little or no frothing occurs after proper digestion.[a]

C. H. Jones, Vermont.—The filtrate after the digestion with neutral permanganate solution was colorless in each case.

With the alkaline permanganate method I am satisfied that the preliminary digestion of thirty minutes or one hour is necessary, not so much that the results may be slightly increased, but that danger from frothing is lessened if not entirely obviated when the distillation begins. It should be noted that it is quite necessary to rotate the flask occasionally during the digestion and distillation if the material shows a tendency to creep up the sides of the flask.

I reground samples Nos. 1, 3, and 4 before making any tests, as the samples containing blood seemed to me too coarse to enable one to get concordant results with the Kjeldahl method.

J. B. Robb, Maryland.—The total nitrogen was determined by the Gunning method and the samples were digested for one hour.

In the alkaline permanganate method the flasks were shaken several times during the process of distillation to prevent the material from adhering to the sides of the flask.

In my opinion the neutral permanganate method is very unsatisfactory, as the results obtained by it are not at all concordant.

F. W. Woll, Wisconsin.—No. 597, S. & S. filters 9 cm were used.

Sample No. 1, blood, washed clear.

Sample No. 2, cotton-seed meal, washed turbid, which necessitated refiltering through double paper (No. 597, S. & S.).

Sample No. 3, washed clear.

Sample No. 4, washed turbid, treated the same as sample No. 2.

Jena 800-cc round-bottom flasks were used for distillation.

A. M. Peter, Kentucky.—It being apparent that all the permanganate was reduced before the digestion was completed, in the alkaline method, an additional quantity of 1.6 grams permanganate dissolved in 100 cc water were added to each of the flasks in set 3 and the distillation repeated, the following additional quantities of nitrogen being obtained: Sample No. 1, 1.25 per cent; No. 2, 1.30 per cent; No. 3, 1.54 per cent; No. 4, 1.40 per cent. At the close of the distillation the liquid in the flasks was still green from excess of manganate.

Another portion of 1.6 grams permanganate and 100 cc water was added to each flask and the distillation was repeated with the following results: Additional nitrogen obtained from sample No. 1, 0.40 per cent; No. 2, 0.20 per cent; No. 3, 0.20 per cent; No. 4, 0.13 per cent.

The total available nitrogen obtained in these three distillations was as follows:

[a] See the Fourteenth Report of the Vermont Experiment Station, p. 219.

Sample No. 1, 3.22 per cent; No. 2, 2.76 per cent; No. 3, 3.08 per cent; No. 4, 3.01 per cent.

Another set of determinations was made, following the referee's directions in every respect, except that 200 cc of alkaline permanganate were used instead of 100 cc. The results were that the following percentages of available nitrogen were obtained: Sample No. 1, 2.24; No. 2, 1.90; No. 3, 2.17; No. 4, 2.10.

Still another series was made, following the referee's directions in every particular, except that the distillation was pushed until the residues in the flasks were dry at the bottom. In this set some parts of the residue may have been overheated, as the flasks were over the direct flame. The results were the following percentages of available nitrogen: Sample No. 1, 2.58; No. 2, 2.16; No. 3, 2.93; No. 4, 1.50.

It appears that there is not enough permanganate in 100 cc of the alkaline solution as prescribed to complete the decomposition. I do not see that either method is giving us available nitrogen, and the alkaline permanganate, as carried out, seems to be especially faulty.

Discussion of Results.

Without discarding any figures on total nitrogen, the differences between maximum and minimum results are, respectively, 0.60 in No. 1, 0.46 in No. 2, 0.36 in No. 3, and 0.40 in No. 4. These discrepancies are large for total nitrogen.

The point mentioned by the referee last year with regard to the time of digestion is brought out here, namely, that the digestion should be prolonged in order to insure the recovery of all the nitrogen.

Setting aside the highest and lowest results we have determinations ranging within less than 0.3 per cent, which is as exact a result as has been obtained in the past.

When the results on the availability of the nitrogen are considered, it is seen that duplicate analyses by any one analyst agree well, taking each method by itself.

Both methods have been evolved from the method of determining albuminoid ammonia in water, as is shown by the first method proposed in the reports of the association.[a] They differ radically in principle, the neutral permanganate being used merely to dissolve the nitrogen, while the alkaline method dissolves it and also transforms it into ammonia.

The critical features of the former method are time and temperature, as in determining citrate soluble phosphoric acid. The latter method possesses the same weakness possessed by Wanklyn's method for albuminoid ammonia—that in the case of vegetable matter it will recover only about one-half of the total nitrogen, and its critical features are the amount of permanganate which will be affected by cellulose and the amount of distillate which is collected.

As is mentioned by Mr. Peter, neither method seems to give the available nitrogen; yet I can think of nothing better. We have in fertilizers about all forms of vegetable and animal proteids, both raw and cooked. Obviously none of the usual solvents for proteids can be employed in this work. We must therefore attempt to use a substitute.

The neutral permanganate method has compared most favorably with vegetation tests in its relative effects on the various nitrogenous fertilizers. On the other hand, the alkaline method is a convenient one for determining whether a fertilizer is easily transformed to ammonia or not.

This method needs to be modified somewhat. If more time had been available, the referee would have tried increasing the amount of solution used in order to have a greater volume for distillation and the regulation of the amount of distillate collected. Reasoning from the practice with albuminoid ammonia in water analysis,

[a] U. S. Dept. Agr., Division of Chemistry Bul. 47.

this latter point would be especially important. Another fact which bears on this point is that in residues after distillation, when washed as in the neutral method and the insoluble nitrogen determined, the nitrogen was found to have been almost totally dissolved, even in a sample of ground leather.

With regard to the neutral method I think that the use of a Witt plate or Hirsh funnel is, as a rule, advantageous in reducing the time and in enabling one to use a smaller filter paper.

I do not think it necessary to make a change in the method of determining total nitrogen, although the weight of evidence is in favor of prolonging digestion for three or more hours. The increase in nitrogen is so slight that it would be negligible in some work, while important in others. The good sense of our station chemists will result in their familiarizing themselves with the work of the association on such a point, after which the character of the work will govern the mode of execution.

I believe that the alkaline permanganate method is worthy of further attention, and that each method should be reduced to a form which will give more closely concordant results.

My only recommendation as a result of this year's work is that the subject be continued by the next referee, with the view of getting more concordant results with each method.

The PRESIDENT. Is there any discussion on this subject? There was a time when this association discussed the papers submitted by referees.

Mr. CAVANAUGH. In determining nitrogen in the Cornell University agricultural experiment station laboratory, both mercuric oxid and potassium sulphate are used. The order of adding the potassium sulphate and sodium hydroxid, as given in the present official method, is reversed. The sodium hydroxid is added first, and the precipitated mercurammonium compound is then decomposed by the potassium sulphate. That complete decomposition takes place has been repeatedly demonstrated by many trials, comparing this modification with the official methods. The advantage gained is in adding the potassium sulphid to an alkaline solution, thereby avoiding an evolution of hydrogen sulphid. The time of digestion is shorter when both mercuric oxid, or mercury, and potassium sulphate are used than with either alone. Distillation with steam has been found very efficient, especially in soil work. No bumping ever occurs even when there is a large amount of precipitate in the distilling flask.

The PRESIDENT. I will now call for the report on sugar.

REPORT ON SUGAR.

By G. L. SPENCER, *Referee.*

The associate referees, Messrs. L. S. Munson and L. M. Tolman, have conducted the experimental work on chemical and optical methods in sugar analysis. No report is presented by Mr. D. L. Davoll, who was appointed to investigate special analytical methods used in the sugar industry.

OUTLINE OF WORK DONE.

I shall present a brief outline of the investigations made, and from these and the results of my own experience in those analytical methods of special importance in

the sugar industry, recommendations will be offered upon optical and chemical methods and upon that part of the work which was allotted to Mr. Davoll.

Mr. Munson's investigations were made with a view to the simplification of the methods for determining reducing sugars and increasing the accuracy of such work. He reviewed the work of many chemists, and conducted analyses for the verification of their results. He made experiments to determine whether the copper in the cuprous oxid obtained in the reduction method can be accurately ascertained from the weight of the suboxid. His results fully demonstrate the accuracy of the method in which the suboxid is directly weighed. Mr. Munson also conducted investigations along the line of devising a single copper solution which could be used with all reducing sugars with a uniform length of time and method of heating. This work has led to no definite conclusions, but the outlook is sufficiently promising to warrant continuing these investigations another year. He also investigated various conditions which modify the reduction. The results of Mr. Munson's investigations will be given in a paper which he will read at the proper time.

The work of Mr. Tolman was in the study of optical methods for the determination of sucrose. Mr. Tolman made experiments to show the effect of varying quantities of acid in the inversion upon given quantities of sugar, and made a study of the effect of these changes upon the factor used in the calculations. He also made a study of inversion at ordinary laboratory temperatures, with a view to simplifying the optical method usually termed Clerget's method.

Mr. Tolman investigated the use of hydrochloric acid in the proportions used in the German official method, in the inversion of sucrose at ordinary temperatures and obtained very satisfactory results. His investigations and the very large amount of work that has been done abroad in the verification of the German official method render it advisable that we adopt it as the official method of this association.

Mr. Tolman also investigated the use of citric acid in the inversion of sucrose, and demonstrated that in the absence of sodium acetate it will give very accurate results. Its advantage lies in not affecting the rotatory power of levulose or decomposing it. This method of inversion is of value in the examination of honeys. Mr. Tolman has prepared a paper for the association, giving his investigations in full.

In the matter of special analytical methods used in the sugar industry, those which should claim the attention of this association are methods relating to the analysis of sugar beets, with a view to fixing their purchase price, and the methods for the analysis of raw sugars.

In our opinion only direct methods of beet analysis need be considered. These methods are divided into two classes, viz, alcoholic and aqueous methods. The alcoholic methods are usually considered the more scientific and are largely employed in sugar-house control. The Germans usually prefer the alcohol methods. The aqueous methods, devised by Pellet, are used almost exclusively in France and Belgium and to a large extent in Germany and in the United States. Owing to the expense incurred in the alcoholic methods for the solvent, and also to the time involved, the water methods and the indirect method are used almost if not quite exclusively in this country in testing beets to fix the purchase price.

The question of the examination of raw sugars has been very thoroughly considered by the Treasury commission and by the committee of the international congress of applied chemistry and we shall base our recommendations largely upon their work.

Recommendations.

The referee and his associates offer the following recommendations for changes in and additions to the official methods and for future work:

(1) To the heading "Determination of water," page 27,[a] add "and density;" after (*a*) insert "water," and after (*b*) change to read "Areometric methods for density and indirect estimation of water."

[a] References are to Bul. No. 46, revised, Div. of Chem., U. S. Dept. of Agr.

(2) Page 28: Insert the following to precede the table:

This method is accurate with liquids containing only soluble carbohydrates. With sirups, molasses, and liquids containing mineral matter, the results are only roughly approximate.

(3) Page 38: Insert the following method for ascertaining the amount of copper reduced, as a provisional method:

(*f*) Method by Direct Weighing of the Cuprous Oxid: Prepare a Gooch crucible for the filtration by loading it with a felt of asbestos one-fourth inch thick. First thoroughly wash the asbestos with water to remove small particles, then follow successively 10 cc alcohol and 10 cc of ether, and dry the crucible and contents thirty minutes in a water oven at 100° C.

Collect the precipitated suboxid of copper in the felt as usual, thoroughly wash it with hot water, then with 10 cc of alcohol, and finally with 10 cc of ether. Dry the precipitate thirty minutes in a water oven at 100° C; cool and weigh it. The weight of cuprous oxid multiplied by 0.888 gives the weight of metallic copper.

(4) Page 39, "Optical methods for the determination of sucrose," omit Clerget's method (page 39) and Creydts' method (page 40), and substitute for them the German official methods, as follows:

Determination of sucrose and raffinose.—This method is not applicable in the presence of optically active bodies other than sucrose and raffinose. Percentages of raffinose less than 0.33 can not be determined with certainty by this method.

Dissolve the normal weight of the material in water, clarify as usual, and dilute to 100 cc. Filter and polarize the filtrate at 20° C. Record the polariscope reading as the direct reading or polarization before inversion.

Dissolve 13.024 grams of the substance in 75 cc of water in a 100-cc flask, and add little by little, while rotating the flask, 5 cc of hydrochloric acid containing 38.8 per cent of the acid; and heat the contents of the flask, after mixing, on a water bath heated to 70° C. The temperature of the solution in the flask should reach 67° to 70° in two and one-half to three minutes. Maintain a temperature of as nearly 69° as possible during seven to seven and one-half minutes, making a total time of heating of ten minutes. Remove the flask and cool the contents rapidly to 20° C., and dilute the solution to 100 cc. Polarize this solution in a tube provided with a lateral branch and a water jacket passing a current of water around the tube to maintain a temperature of 20° C.

Multiply the invert reading, made at 20° C. by 2. If a preliminary calculation using the formula,

0.7538X (algebraic difference of the direct and invert readings)=per cent sucrose,

gives a percentage which is more than 1 per cent higher than the direct reading, raffinose is probably present, and the following formulæ by Creydt should be used:

P—the direct reading.
I—the invert reading.
S—the percentage of sucrose.
R—the percentage of anhydrous raffinose.

$$S=\frac{0.5188P-I}{0.8454};\ R=\frac{P-S}{1.85}.$$

Determination of sucrose in the absence of raffinose.—The inversion and observation should be made as described above and the following formula used:

When the polarizations are made at 20° C.:

$$S=\frac{100\ (P-I)}{142.66-\frac{20^\circ}{2}}=0.7538X\ (P-I).$$

Should the temperature (t) vary from 20°, which is permissible within narrow limits, in the absence of raffinose use the following formula:

$$S=\frac{100\ (P-I)}{142.66-\frac{t}{2}}.$$

It is recommended that it also be permissible to conduct the inversion as follows:

Prepare the solutions as described above, using 50 cc of water instead of 75 cc and employing the proportion of acid specified, and set the flask aside during a period of twenty-four hours at a temperature of not below 20° C.; or if the temperature be above 25° set aside ten hours.

(5) For the direct analysis of sugar beets we recommend that the following be inserted as provisional methods:

(*a*) *Scheibler's alcoholic method.*—In the direct analysis of the beet with the Soxhlet-Sickel apparatus by Scheibler's method, proceed as follows for the extraction of the sucrose:

Place a plug of absorbent cotton in the bottom of the tube, then introduce 26.048 grams of the pulped beet, or 2×16.29 grams, according to the polariscope in use, pressing the pulp lightly with a rod. Very small fragments of the beet may be used instead of pulp. Connect the extractor with the reflux condenser. Place 75 cc of 95 per cent alcohol in the flask and connect with the extractor; heat the flask in the water bath and continue the extraction from half an hour to two hours or more, according to the state of division of the sample. Use somewhat weaker alcohol if only 16.29 grams of pulp be taken. Cool and remove the flask, substitute a second containing 75 cc of 75 to 80 per cent alcohol, and continue the extraction to ascertain whether the first extraction were complete.

Fill the first flask to the 100-cc mark, after treating the sample with two or three drops of subacetate of lead solution. Mix the contents of the flask, filter, and polarize. Having extracted the normal weight of pulp, the polariscopic reading is the per cent of sucrose in the sample.

The extract in the second flask should also be polarized as a check upon the extraction.

Great care is essential in the polarization of alcoholic solutions. The least quantity of subacetate of lead that will clarify the solution should be used. The solution must be protected from evaporation during the filtration by a cover glass. Avoid irregularities in the temperature of the solution in the observation tube, due to the warmth of the hands; since the density of the solution in different parts of the tube will vary under such conditions, striæ will form, rendering an accurate reading impossible.

The Scheibler method, as above described, differs from the original only in a few minor details, especially in the arrangement of the extraction apparatus. The Soxhlet extraction apparatus is much more effective than Scheibler's original instrument.

(*b*) *Pellet's aqueous method—Hot digestion.*—Any good rasp may be used in the preparation of the pulp for this method. The special flasks with enlarged necks are convenient for use in this method. Transfer 26.048 grams of the pulp to the flask, using a little water to wash the weighing capsule and funnel; or, for the Laurent, employ 32.58 grams of pulp, i. e., $2 \times$ normal weight. The flasks are graduated to contain 201.35 cc for the Schmidt and Haensch and 201.7 cc for the Laurent polariscopes, in order to compensate for the volume of the marc and the lead precipitate. Add 5 to 10 cc subacetate of lead solution of 54.3° Brix for the clarification. Approximately 6 to 7 cc are required per 26 grams of beet pulp. This reagent should be run into the flask in advance of the beet pulp. Add a few drops of ether to beat down the foam, then sufficient water to increase the volume of the solution to about 190 cc. Heat to 80° C. in a water bath and maintain this temperature about thirty minutes, occasionally giving the flask a circular movement to facilitate the escape of the air from the pulp. Increase the volume of the solution from time to time during the heating, so that when the operation is completed only a few drops of water will be required to complete the volume of the solution to the mark. After approximately thirty minutes' heating, cool the flask and contents and add strong acetic acid to the solution to acidity, dilute to the graduation, mix, and filter. The state of division of the pulp will govern the time of heating. In polarizing the filtrate, use a 400-mm. observation tube, thus directly obtaining the per cent sucrose in the beet with the Schmidt and Haensch polariscope, or double this percentage if the Laurent instrument be used.

(6) For the analysis of sugars we recommend that the methods selected by the international committee for unifying methods of sugar analysis be adopted as provisional methods of this association. These methods are as follows:

1. In general, all sugar tests shall be made at 20° C.

2. The graduation of the saccharimeter shall be made at 20° C. Twenty-six grams of pure sugar, dissolved in water, and the volume made up to 100 metric cc, or during the period of transition 26.048 grams of pure sugar in 100 Mohr cc, all weighings to be made in air with brass weights, the completion of the volume and the polarizations to be made at 20° on an instrument graduated at 20° should give an indication of 100 on the scale of the saccharimeter. For countries where temperatures are usually higher than 20° C., it is permissible that saccharimeters be graduated at 30°, or any other suitable temperature, under the conditions specified above, provid-

ing that the analysis of the sugar be made at the same temperature—that is, that the volume be completed and the polarizations made at the temperature specified.

3. Preparation of pure sugar: Purest commercial sugar is to be further purified in the following manner: A hot saturated aqueous solution is prepared and the sugar precipitated with absolute ethyl alcohol; the sugar is carefully spun in a small centrifugal machine and washed in the latter with absolute alcohol. The sugar thus obtained is redissolved in water, the saturated solution again precipitated with alcohol and washed as above. The product of the second crop of crystals is dried between blotting paper and preserved in glass vessels for use. The moisture still contained in the sugar is determined and taken into account when weighing the sugar which is to be used.

The committee further decided that central stations shall be designated in each country which are to be charged with the preparation and distribution of chemically pure sugar. Wherever this arrangement is not feasible, quartz plates, the values of which have been determined by means of chemically pure sugar, shall serve for the control of the saccharimeters. The committee further decided that the above control of quartz plates by means of chemically pure sugar should, as a rule, apply only to the central stations which are to test the correctness of saccharimeters; for those who execute commercial analyses, the repeated control of the instruments is to be accomplished, now as before, by quartz plates.

4. In effecting the polarization of substances containing sugar, half-shade instruments, or triple field, only are to be employed.

5. During the observation the apparatus must be in a fixed position and so far removed from the source of light that the polarizing nicol is not warmed.

6. Sources of light may be gas, triple burner with metallic cylinder, lens and reflector; gas lamps with Auer (Welsbach) burner; electric lamp; petroleum duplex lamp; sodium light. Several readings are to be made and the mean thereof taken, but any one reading must not be neglected.

7. In making a polarization, the whole normal weight for 100 cc is to be used, or a multiple thereof for any corresponding volume.

8. As clarifying and decolorizing reagents there may be used: (*a*) subacetate of lead (3 parts by weight of acetate of lead, 1 part by weight of oxid of lead, 10 parts by weight of water); (*b*) alumina cream; (*c*) concentrated solution of alum. Bone-black and decolorizing agents are to be excluded.

9. After bringing the solution exactly to the mark, at the proper temperature, and after wiping out the neck of the flask with filter paper, all of the well-shaken clarified sugar solution is poured upon a dry rapidly acting filter. The first portions of the filtrate are to be rejected and the rest, which must be perfectly clear, used for polarization.

(7) For future investigations we recommend a continuation of the studies along the lines of those of this year.

The PRESIDENT. Are there any papers on this subject for presentation?

Mr. MUNSON. I have a paper on sugar to submit to the association.

METHODS FOR DETERMINING REDUCING SUGARS.

By L. S. MUNSON.

METHODS IN USE.

The methods now used by this association for the determination of reducing sugars are: (1) an approximate volumetric method for rapid work; (2) Soxhlet's volumetric method for more exact work; (3) Herzfeld's method for analysis of mixtures containing less than 1 per cent of reducing sugar; (4) Meissl and Hiller's method for analysis of mixtures containing from 1 per cent to 100 per cent of reducing sugars; (5) Allihn's method for the determination of dextrose; and (6) Soxhlet's method for the determination of milk sugar. No method has ever been accepted by the association for the determination of maltose.

The methods for invert sugar and dextrose were adopted at the ninth annual meeting of the association, and have been used to the present time without any modifica-

tion. Soxhlet's method for milk sugar was adopted at a later date, and is, without modification, the method devised by Soxhlet in 1880. The volumetric methods are but little used, except in sugarhouse control, where rapidity is essential. The gravimetric methods for both invert sugar and dextrose are so extensively used in agricultural chemical analysis that it was thought advisable to spend the time of the associate referee in work upon these methods. In outlining this work with the referee, it was decided that an attempt should be made to devise a common method for all the reducing sugars, and to construct tables giving values of the reduced copper in terms of the various sugars. Such a method would greatly simplify the reducing sugar proposition by doing away with the necessity of having different solutions for each of the reducing sugars, and in case of mixtures it would afford a more satisfactory basis for calculating proportional amounts of the different sugars.

Soxhlet's modification of Fehling's solution is used for all the official methods except Allihn's method for dextrose, in which case Allihn's modification of Fehling's solution is used. The concentration of the copper solution is the same for both the modifications as for the original Fehling solution, viz, 34.64 grams of pure crystallized copper sulphate per 500 cc. Fehling's alkaline tartrate was made by using 55 to 64 grams of sodium hydrate and 173 grams of Rochelle salts per 500 cc, while Soxhlet's modification requires 50 grams of sodium hydrate and Allihn's modification 125 grams of potassium hydrate per 500 cc. In my experience Fehling's solution when made up with sodium hydrate gives a more satisfactory precipitation than when potassium hydrate is used, and this alkali is much more commonly employed than potassium hydrate. Glendenning [a] has studied the effect of the two alkalies, when used in equivalent amounts, upon the quantity of copper reduced, and he finds that both dextrose and invert sugar give practically the same reducing power with the two alkalies. Maltose, on the other hand, shows a reducing power of 62 with soda solution and 65 with potash solution. Kjeldahl [b] has studied the effect of a variation of the strength of the soda solution upon the reduction, and finds that between limits of one-half and double the normal weight of soda solution the variation was not more than 1 per cent with dextrose and reducing sugar, while with lactose and maltose there was a wide variation, as the following table shows:

TABLE I.—*Effect of varying soda solutions upon reduction.*

Kind and weight of sugar.	Soda solution used.	Copper reduced.
		Mg.
150 milligrams lactose	50 cc solution containing 130 grams NaOH per liter	198.4
	50 cc solution containing 65 grams NaOH per liter	207.2
	50 cc solution containing 32.5 grams NaOH per liter	214.7
360 milligrams maltose	50 cc solution containing 50 grams NaOH per liter	411.7
	50 cc solution containing 78 grams NaOH per liter	396.9
220 milligrams dextrose	50 cc solution containing 50 grams NaOH per liter	412.6
	50 cc solution containing 78 grams NaOH per liter	411.0

There seems to be no reason why the copper and alkaline tartrate solutions should not be of the same composition for the various sugars, since the formula must of necessity be an empirical one.

The conditions under which the reduction takes place are of particular importance, and much of the work this year has consisted in a study of these conditions. Recently a number of valuable papers have been published that have a direct bearing upon this subject, and results of some of these investigations will be given as a part of this report.

[a] Jour. Chem. Soc., 1895, p. 999.

[b] Compte-rendu des travaux du laboratoire de Carlsberg, 1895.

EFFECT OF TIME AND MANNER OF HEATING.

O'Sullivan [a] was the first to carry on the reduction in a boiling-water bath instead of heating directly over a free flame; and this method is now quite generally used among English chemists. Brown, Morris, and Millar [b] have determined the cupric reducing power of dextrose, invert sugar, and levulose by heating at the temperature of boiling water for twelve minutes. These values are considerably higher than when the reduction is made by boiling over a free flame for two minutes.

Kjeldahl [c] in an elaborate series of experiments has determined the copper reducing power of dextrose, invert sugar, levulose, maltose, lactose, and galactose by carrying on the reduction in an atmosphere of hydrogen, and continuing the time of heating for twenty minutes from the time the mixed solutions are placed in the water bath. The following table of compiled data shows the reducing values for dextrose and invert sugar obtained by the three different methods of manipulation:

TABLE II.—*Reducing values for dextrose and invert sugar obtained by three different methods.*

Sugar.	Dextrose.			Invert sugar.		
	Copper by boiling 2 minutes. [a]	Copper by heating in water bath 12 minutes. [b]	Copper by heating in water bath 20 minutes. [c]	Copper by boiling 2 minutes. [d]	Copper by heating in water bath 12 minutes. [b]	Copper by heating in water bath 20 minutes. [c]
Mg.	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*
50	98.2	103.0	111.4	96.0	97.5	105.6
75	147.2	154.3	163.2	142.8	146.8	155.6
100	195.0	202.7	212.5	188.8	194.1	203.4
125	242.0	249.6	259.2	233.2	240.0	249.0
150	288.2	293.4	303.3	276.8	283.2	292.3
175	333.4	335.0	345.0	318.8	325.1	333.7
200	377.5	374.5	384.0	360.4	365.0	372.7

[a] Figures taken from Allihn's table for dextrose.
[b] Figures taken from tables by Brown, Morris and Millar.
[c] Figures taken from Kjeldahl's tables.
[d] Figures taken from Meissl's table for invert sugar.

The values obtained by Kjeldahl are much higher than those obtained by either of the other methods, owing partially to the longer time of heating, but principally to the fact that the reduction was made in an atmosphere of hydrogen, and consequently no oxidation took place during the period of heating.

I have also conducted a series of experiments with dextrose and invert sugar in which the time of heating in a water bath was varied between five minutes and twenty minutes. The following are the results:

[a] Jour. Chem. Soc. Trans., **2**: 125 (1876).
[b] Jour. Chem. Soc. Trans., 1897, p. 275.
[c] Compte-rendu des travaux du laboratoire de Carlsberg, 1895.

TABLE III.—*Copper reduced upon heating in boiling water bath for varying periods.*

Sugar.	Manner and time of heating.	Copper reduced.	Increase in copper for 5-minute periods.
Dextrose (milligrams).		*Milligrams.*	*Milligrams.*
150.3	Boiled 2 minutes	286.5	.....
150.3	Heated in boiling water [a] 5 minutes	281.0	.....
150.3	Heated in boiling water [a] 10 minutes	286.5	5.5
150.3	Heated in boiling water [a] 15 minutes	289.4	2.9
150.3	Heated in boiling water [a] 20 minutes	292.8	3.4
Invert sugar (milligrams).			
162.8	Boiled 2 minutes	303.5	.....
162.8	Heated in boiling water [a] 5 minutes	298.4	.....
162.8	Heated in boiling water [a] 10 minutes	303.2	4.8
162.8	Heated in boiling water [a] 15 minutes	307.1	3.9
162.8	Heated in boiling water [a] 20 minutes	310.5	3.4

[a] The sugar was added to the cold Fehling solution, and time was counted from the moment the mixture was placed in the boiling water bath.

The above figures show that the method of boiling for two minutes over a direct flame gives results practically identical with heating for ten minutes in a boiling-water bath.

One advantage claimed for the method of heating in a boiling-water bath is that after heating for 10 to 15 minutes the reduction is practically completed, and upon further heating the amount of reduction that takes place is exceedingly small. Table III shows that this is not the case, but that after fifteen minutes' heating five minutes additional heating gave 3.4 milligrams of copper. Kjeldahl found in his work that upon heating for twenty minutes there was a material spontaneous precipitation of copper, which greatly augmented when the time of heating was prolonged. The following table shows results obtained by myself when the period of boiling over a direct flame was varied between just bringing to a boil and four minutes' boiling:

TABLE IV.—*Copper reduced upon boiling over free flame for varying periods.*

Sugar.	Time of heating.	Copper precipitated.	Increase in copper.
Dextrose (milligrams).		*Milligrams.*	*Milligrams.*
250	Brought to boil	437.2	.....
250	Boiled 2 minutes	439.5	2.3
125	Brought to boil	227.9	.....
125	Boiled 2 minutes	229.8	1.9
Invert sugar (milligrams).			
185.9	Brought to boil	245.1	.....
185.9	Boiled 1 minute	346.8	1.7
185.9	Boiled 2 minutes	347.6	0.8
185.9	Boiled 3 minutes	348.7	1.1
185.9	Boiled 4 minutes	350.4	1.7

The increase in the amount of copper reduced for each additional minute's boiling is higher somewhat than when heating in boiling water is employed, but the difference is not sufficient to give any preference to either method.

In an effort to verify Kjeldahl's statement that appreciable amounts of copper are precipitated upon heating the Fehling solution, I found that only traces were precipitated when the solution was heated for twenty minutes in boiling water. Heating over a direct flame gave no reduction upon two minutes' heating, 2 milligrams upon four minutes, 5.6 milligrams upon six minutes, and 8.5 milligrams upon eight minutes' boiling. However, different solutions undoubtedly vary in this respect, depending upon the length of time the alkaline tartrate solution has been made up. In all cases, whatever method is used, the amount of copper precipitated spontaneously should be determined and deducted from the amount obtained in the sugar determinations.

Effect of Surface Exposed During Reduction.

But few if any of the reducing sugar methods prescribe a receptacle of definite size for the reduction. While beakers of varying sizes are generally employed, Erlenmeyer flasks, and even porcelain dishes, are occasionally used. Kjeldahl has studied the effect upon the amount of copper reduced of the surface of liquid exposed when dishes of different sizes are used for the reduction, and he gives the following interesting results:

Table V.—*Effect of amount of surface exposed to the air upon the copper reduced.*

Sugar.	Surface exposed to air	Copper reduced.	Difference.
Milligrams.	*Sq. cm.*	*Milligrams.*	*Milligrams.*
60	(*a*)	126.3	.....
60	2	126	0.3
60	17	123.9	2.4
60	21	121.5	4.8
60	65	114.8	11.5
60	186	106.6	19.7

a None; reduction in hydrogen.

In all the experiments of Kjeldahl the time of heating was twenty minutes. I have conducted a similar series of experiments, the results of which are given below in Table VI:

Table VI.—*Effect of surface exposed to the air upon the copper reduced under varying conditions of manipulation.*

Invert sugar.	Receptacle used.	Surface exposed.	Manner and time of heating.	Copper reduced.	Difference.
Mg.		*Sq. cm.*		*Mg.*	*Mg.*
150.5	Erlenmeyer	(*a*)	Boiled 2 minutes	284.2	.....
150.5	do	(*b*)	do	284.5	.....
150.5	Beaker	40	do	281	3.4
150.5	Erlenmeyer	(*a*)	Heated 15 minutes in boiling water.	291.7	.....
150.5	do	(*a*)	do	290.6	.....
150.5	Beaker	40	do	286.7	4.5
168.5	Erlenmeyer	26.5	Boiled 2 minutes	313.7	.....
168.5	Small beaker	26.5	do	313.9	.....
168.5	Beaker	40	do	313.4	.5
168.5	Erlenmeyer	26.5	Heated 15 minutes in boiling water.	320	.....
168.5	Small beaker	26.5	do	320.1	.....
168.5	Beaker	40	do	317.2	2.8

a None; reduced in CO_2. *b* None; reduced in hydrogen.

It is seen from Tables V and VI that the greater the surface of liquid exposed to the air during the reduction the less is the amount of copper reduced. In other words, the oxidation of the cuprous oxid by exposure to the air is very marked. In Kjeldahl's series of experiments the amount of copper varied by an extreme difference of 19.7 mgs with receptacles ranging in surface exposed from none to 186 sq. cm. While it is hardly probable in ordinary work that the reduction would be made in a dish giving an exposed area of 186 sq. cm., it is undoubtedly true that dishes giving from 15 to 65 sq. cm exposed surface are frequently employed. I have found that a beaker 7.5 cm in diameter is of very convenient size for making the reduction, and have used this size in all my regular work. It appears from Table VI that the amount of oxidation is greater when the reduction is conducted in a boiling-water bath, heating for fifteen minutes, than when the reduction is made by boiling over a free flame for two minutes. In the first series the amount of oxidation is greater by 1.1 mg. when reduced in boiling water for fifteen minutes; and in the second series the amount of oxidation is greater by 2.3 mg of copper when heated in boiling water for fifteen minutes, when the surface exposed is increased from 26.5 to 40 sq. cm. The method employed by Kjeldahl of conducting the reduction in an atmosphere of hydrogen undoubtedly gives more nearly the true reduction than any other method yet employed, but the inconveniences attending such a manipulation would preclude its general use.

Determination of Copper by Weighing the Cuprous Oxid.

The determination of copper by direct weighing of the cuprous oxid was first suggested by O'Sullivan and Stern,[a] who state that results obtained by this method are as accurate as given by the methods ordinarily used. In 1900 Knight reported to this association results of a series of experiments showing that this method of determining the copper checks up very closely with the electrolytic method. It has been our experience in the laboratory of the Bureau of Chemistry, where we have practiced direct weighing of the cuprous oxid for the past two years, that the method gives reliable results, and that the determination is much more easily made than by any of the official methods of this association. I have made a number of determinations checking this method with the electrolytic method, results of which are given in Table VII.

Table VII.—*Comparison of the method of direct weighing of cuprous oxid with electrolytic method.*

Weight of copper.		Difference in weight.	Weight of copper.		Difference in weight.
By weighing as Cu_2O.	By electrolysis.		By weighing as Cu_2O.	By electrolysis.	
Mg.	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*
440.0	439.6	−0.4	319.9	320.1	+0.2
437.2	437.8	+ .6	316.7	317.2	+ .5
227.9	229.1	+1.2	317.7	316.5	−1.2
229.5	230.9	+1.4	284.9	284.0	− .9
447.7	448.0	+ .3	282.2	281.0	−1.2
447.3	447.3	0.0	290.0	288.8	−1.2
320.5	321.4	+ .9	286.9	286.9	0.0
278.4	278.3	− .1	287.8	288.0	+ .2
279.2	280.6	+1.4	303.6	303.9	+ .3
278.0	278.2	+ .2	303.4	303.3	− .1
233.6	235.4	+1.8	289.5	289.5	0.0
460.4	460.5	+ .1	298.3	298.8	+ .5
459.5	460.3	+ .8	303.2	303.7	+ .5
316.7	317.2	+ .5	303.2	302.4	− .8
312.1	313.4	+1.3	Average..	.....	+ .22

[a] Jour. Chem. Soc. Trans., 1896, p. 1691.

Upon 29 determinations the electrolytic method gives results averaging 0.22 mgs higher than by weighing as cuprous oxid, and the differences by the two methods vary between —1.2 and +1.8 mgs. A small amount of asbestos is dissolved by the hot Fehling solution during filtration, and in the recorded experiments this factor was not taken into consideration. If the asbestos is carefully prepared by first digesting with 1:3 hydrochloric acid and then with Fehling's solution, the amount of asbestos dissolved upon filtering the hot Fehling solution need not exceed 0.3 to 0.5 mgs. Should this correction be added to results obtained by weighing the cuprous oxid, the two methods would check very closely. I have found it convenient to dissolve off the cuprous oxid with hot nitric acid after each determination, and in this way the same felt of asbestos may be used several times.

The method of weighing the cuprous oxid is conducted as follows: Load a Gooch crucible with a film of asbestos about one-fourth of an inch thick; wash thoroughly with water to remove small particles of asbestos, then with about 10 cc of alcohol, and finally with 10 cc of ether. Dry in a water oven at 100° C. for twenty-five to thirty minutes, and cool for one-half hour before weighing. After filtering the cuprous oxid into the Gooch and washing thoroughly with water, the precipitate and Gooch are washed with 10 cc of alcohol and then with 10 cc of ether as in the preparation of the Gooch. Dry for twenty-five to thirty minutes in water oven at 100° C.; cool for one-half hour and weigh. The weight of cuprous oxid multiplied by 0.888 gives weight of metallic copper. It has been my experience that twenty-five to thirty minutes heating at 100° is sufficient to thoroughly dry the precipitated cuprous oxid and asbestos without danger of the suboxid undergoing oxidation, providing the washing with alcohol and ether has been thorough.

Mr. Wiley. I would like to suggest that Mr. Gudeman's paper on the "Determination of glucose," which was to be submitted to the association, be returned to him for further elaboration, and that after such modification it be incorporated in the proceedings of this meeting.

The President. If there is no objection, the paper will be returned to Mr. Gudeman for further consideration and then be included in the proceedings. The secretary is so instructed.

THE DETERMINATION OF GLUCOSE.

By Edward Gudeman, *Chicago, Ill.*

The method used for the determination of commercial glucose is the one given in the provisional methods of the Association Official Agricultural Chemists, 1901. The method consists in polarizing before and after inversion, calculating the per cent of sugar "S" by Clerget's formula and inserting this value in the following formula:

$$G=\frac{(a-S)\ 100}{175}$$

G=Commercial glucose.
a=Direct polarization.
175=Polarization factor for commercial glucose.

The use of this factor (175), or any other factor between 80 and 198, will give incorrect results, a correct result being purely accidental. It is only in laboratory work that one has the same substance to experiment with that has been used in making up the mixtures under examination and on which a correct factor for that special glucose or grape sugar can be determined.

One is often at sea as to what is meant by the term commercial glucose. In England the terms glucose and grape sugar are synonymous, the sirup being designated as

liquid glucose. In America the term glucose refers only to the sirup, the solid being designated as grape sugar. The reducing substances of glucose and grape sugar are commercially, but incorrectly, known as "dextrose" and the nonreducing substance as "dextrins." The composition of commercial glucose and grape sugar varies between wide limits, the extremes being about as follows:

Glucose { Reducing substance 40 to nonreducing substance 60; ratio 6 : 9.
Reducing substance 55 to nonreducing substance 45; ratio 11 : 9.

Grape sugar { Reducing substance 80 to nonreducing substance 20; ratio 36 : 9.
Reducing substance 92 to nonreducing substance 8; ratio 103.5 : 9.

Glucose is a thick sirup, 41° to 45° Baumé, containing 13 to 22.5 per cent of water. Grape sugar is a solid, 41 to 45° Baumé, containing 11 to 21.0 per cent of water. The old standard Baumé scale is still used in this industry, and the determinations are made at 140° F., results reported at 100° F., a correction of 1 degree being made for every 40° F. The standard accepted by the manufacturers and the trade is sp. gr. 1.41152=42° Baumé.

The conversion of starch with acids gives the commercial products known as dextrin, glucose, grape sugar, and anhydrous grape sugar (dextrose). Starch and its conversion products do not contain over 1 per cent impurities, and, as these have little or no effect on the polarization nor on the copper reduction, they have not been taken into consideration. All results are calculated on the sum of the reducing and nonreducing substances being equal to 100. All results are figured on the amount of dry substance contained in the mixtures.

If the conversion of starch with acid is carried to a point where a dilute iodin solution will just give a distinct color reaction, we have glucose; continued to where 95 per cent alcohol gives a faint cloud, hardly a precipitate, we have grape sugar containing about 85 per cent reducing substance. For still higher converted sugars a time factor must be introduced. Carried beyond a given point a back conversion takes place, with strong decomposition and loss of purity.

The ratio of the reducing substance to nonreducing substance depends on the accuracy in stopping the conversion, for neutralization, at the exact point decided upon. This ratio determines whether the product is glucose or grape sugar, and no sharp dividing line exists. The rotating powers of glucose and grape sugar depend absolutely on this ratio. Actually no two batches of commercial glucose or grape sugar are identical; for all practical purposes they are alike, as a few points either way from the standard decided upon will make no difference in the appearance, taste, or working qualities of these products.

The conversion of starch does not take place in direct steps; immediately when the starch is liquefied it passes into the various conversion products. At no point of the conversion is a single product, either of dextrin or dextrose obtained. The rotation of dextrin and dextrose can easily be determined on the pure products separated from the mixture. At no point of the conversion do you obtain the extreme polarization figures, 230 for maize dextrin, and 80 to 153 for maize dextrose. The accompanying graphic chart (fig. 1) shows the polarization and the percentage of nonreducing and reducing substances for the following commercial products: Glucose, grape sugar, dextrose, and chemically pure dextrose.

The first commercial product in the acid conversion is glucose: Line ab: Reducing substance 40 to nonreducing substance 60. Line abc: Reducing substance 55 to nonreducing substance 45.

The second product is grape sugar: Line abcd: Reducing substance 80 to nonreducing substance 20. Line abcde: Reducing substance 92 to nonreducing substance 8.

The final commercial product, anhydrous grape sugar (dextrose), passes through the glucose and grape-sugar stages: Line abcdefg to abcdefgh. Dextrose is birotary

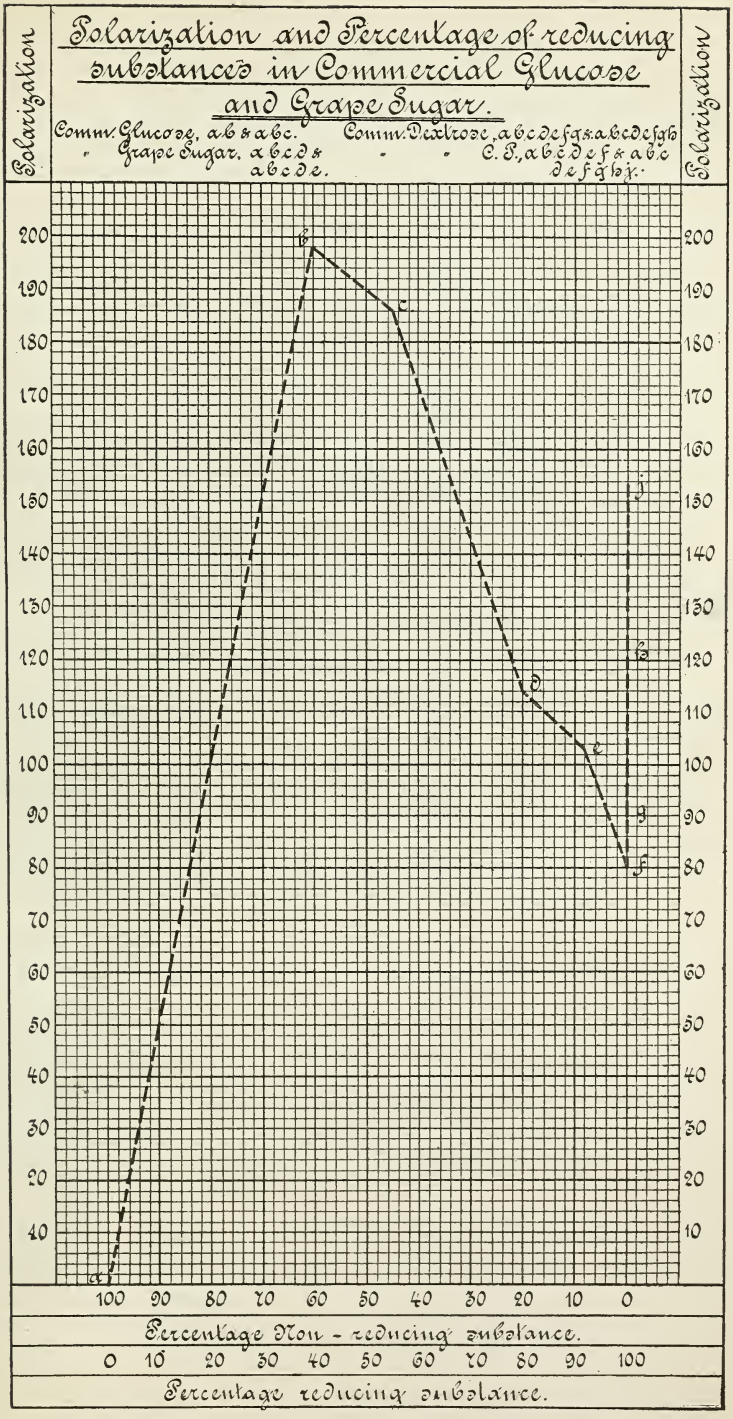

FIG. 1.—Polarization of commercial glucose and grape sugar and percentage of reducing substances therein.

and as the rotation of the commercial product is higher than that of grape sugar, there is no doubt that it must have passed through the lowest point for dextrose before going up again. The high point is only obtained on specially prepared chemically pure dextrose. The rotation of dextrose is birotary, the low point being reached after a comparatively long time in cold solution, but more rapidly on heating to boiling. Under these conditions it is not possible to have a high rotating dextrose in the starch conversion liquor, as the same has been exposed to high temperature, being converted under steam pressure.

The provisional methods state that commercial glucose used for mixing with jams and jellies polarizes at 150, that used for chewing gums at 185, and that used with honeys, sirups, and molasses at 175, and it is suggested to use these values when examining such products. I have never known the manufacturers of glucose to make special grades for these purposes, except for the confectioner, and this grade differs only from the regular glucose by the larger amount of acid salt it contains (bisulphite of soda). The use therefore of different factors of rotation, subject to the samples under examination, will lead to greater errors than the use of a constant (175), even if the same is not correct. Depending on what factor is used, a mixture containing 20 per cent commercial glucose can show from 14.4 to 27.7 per cent, a possible error of 35 per cent. Commercial grape sugar rotating 85 to 190 will show from 43.5 to 225 per cent, depending on the factor used, a possible error of 125 per cent. The addition of cane sugar or invert sugar to such mixtures can cause the polarization figures to become so abnormal, as to be hardly a qualitative indication of the presence of glucose or grape sugar.

On mixtures of which the percentage composition was known, as also the correct rotating power of the component parts, the following results were obtained, applying the formula given in the provisional methods, 1901:

I. With a mixture containing grape sugar 10 per cent, invert sugar 25 per cent, and cane sugar 65 per cent, $a=65$ and $b=-22$. Applying the formula, we find that the grape sugar=0 per cent, an error of 100 per cent.

II. With a mixture containing grape sugar 28.5, invert sugar 6.5, and cane sugar 65 per cent, $a=87$ and $b=0$. By the formula grape sugar=25.8 per cent, an error of 9.6 per cent.

III. With a mixture containing grape sugar 15, invert sugar 20, and cane sugar 65 per cent, $a=71$ and $b=-16$. Applying the formula, grape sugar=7.1 per cent, an error of 52.7 per cent.

IV. With a mixture of 40 per cent grape sugar and 60 per cent invert sugar, $a=13.6$, and $b=13.6$. Applying the formula, grape sugar=17 per cent, an error of 57.5 per cent.

Similar results were obtained with glucose and mixtures of glucose and grape sugars. These errors were found when using the correct factor for the rotating power of the commercial grape sugar. When the correct polarization factor is not known, the errors are increased or decreased, and in some cases may exactly balance each other, when accidentally the application of the formula will give the correct result. This is not a theoretical consideration, as it has a direct bearing on the analyses of sirups, honeys, preserves, jams, candies, molasses, wines, maple sugars, and similar saccharine food products.

Plus polarization before and minus after inversion is generally considered as indicating the absence of commercial glucose or grape sugar. This is not necessarily the case, Mixtures I and III showing plus 65 and 71 before inversion, and minus 22 and 16 after inversion, with 10 to 15 per cent grape sugar present. Mixtures of commercial glucose or grape sugar with invert sugar can show a direct minus reading, increased strongly after inversion if cane sugar is also present.

The quantitative determination of commercial glucose or grape sugar can easily and quickly be made without use of the polariscope and variable factor. If invert

sugar is present, the same must be determined by double polarization. All results are calculated on the basis of the dry substance found in the mixture.

In mixtures free from invert sugar:

I. Determine total directly reducing sugars=a (from glucose or grape sugar).

II. Determine cane sugar by reduction after inversion at 67° C.=b (or Clerget's method calculating reducing power=b).

III. Invert with malt and determine total reducing sugars=c (as in determination of starch).

$c-(a+b)\times 0.932=d$.

d=nonreducing substance from glucose or grape sugar.

a+d=glucose or grape sugar, depending on ratio of a:d.

If invert sugar is present, it must be determined by double polarization at 20° and 87° C.=i.

a—i=A, reducing substance from glucose or grape sugar.

$c-(a+b+i)\times 0.932=d$.

A+d=glucose or grape sugar, depending on ratio of A:d.

The error due to use of factor 0.932 is very small—not over 1 per cent—on a pure low converted glucose containing 60 per cent nonreducing substance. If the mixtures contain starch, same must be separated by cold filtration. Starch in solution will be determined and reported as part of the nonreducing substance. The iodin test will show the presence of starch.

Results by this method are generally low, due, no doubt, to the decomposition of cane or invert sugars present. The larger the percentage of glucose or grape sugar in the mixtures the more accurate the results. The error is never over 3 per cent of the amount of glucose or grape sugar present, averaging about 1 per cent. Duplicates will agree to within 0.2 per cent.

If the mixtures contain no cane nor invert sugars, the malt treatment can be replaced by a direct acid conversion at high temperature. This is not advisable, as other substances (fiber, gums, etc.) will be partly converted into reducing substances. Mixtures of glucose with grape sugar will be indicated by the abnormal ratio of a or A:d being between 11 and 36:9, but for all practical purposes such mixtures can be considered as high converted glucose or low converted grape sugar.

CLERGET'S METHOD AND MODIFICATIONS.

By L. M. Tolman.

At the twelfth annual meeting of this association, Mr. Ewell, then reporter on sugar, recommended that the Clerget and Lindet methods for determination of sucrose be dropped as official methods, and that the German official method, at that time one of the official methods, be made the official method of this association. For some reason not given in the proceedings this was not done, but the German method and the Lindet methods were dropped as official methods and the Clerget retained. The reporter on sugar at the seventeenth annual meeting recommended that a study be made of the Clerget and German methods. That has, therefore, been the line of work attempted by the associate referee this year.

The Clerget method, as now used by this association, is a modification of the original method proposed by Clerget, in that 26.048 grams of sucrose dissolved in 100 cc polarize 100 degrees on the sugar scale, while Clerget used the French normal weight, then 16.471 grams per 100 cc. In every other particular the original method is followed, and the factor determined by Clerget is used.

When Clerget's method is exactly followed and 16.471 grams of sugar are used, his results are correct, and his factor 144 should be used; but when 26.048 grams of sugar are used this factor is too low, owing to the increased concentration. Ross reported at the ninth annual meeting of this association as high a factor as 145.2, using 26.048

grams of sugar, but inverting in a slightly different manner from that prescribed by Clerget. Bornträger[a] obtained as high a factor as 134.98 at 20° C., using 26.048 grams, and, following Clerget's method exactly with this exception, he obtained the factor 144.65, showing that the factor of Clerget is too low for the official method.

Of late years very little has been done to determine exactly the proper factor, all of the investigations having been conducted along the lines of the German method. Herzfeld[b] found that the factor regularly increased in ratio with the increased concentration. The factor determined for 1 gram sugar in 100 cc was 141.85, if the German official method was used in inversion, and it increased to 142.66 for 13 grams of sugar, 143.13 for 20 grams, and to 143.94 for 26 grams. From this investigation Herzfeld derived the following formula for determining the factor for any concentration:

$$S = \frac{(A-B)\ 100}{141.85 + 0.05\,B - \frac{T}{2}}$$

S = sucrose
A = direct polarization
B = invert polarization
T = temperature.

To 141.85, which is the factor for 1 gram of sugar in 100 cc, there is added 0.05 of the invert reading. This formula applies only when the Herzfeld method of inversion is followed. When the official method of this association is followed with the increased amount of acid (10 cc to 110 cc), the increase in the factor due to concentration is larger.

In a paper published in the Journal of the American Chemical Society for June, 1902, I showed that the increment of the factor was 0.062 of B, or the invert reading. This would make the factor 144.44 for 26.048 grams, giving a variation of from 141.85 to 144.44 for different weights of sugar from 1 gram to 26 grams, while with the German method there is a variation of from 141.85 to 142.66. The latter method, therefore, is more accurate, unless the factor is calculated for each concentration, as proposed by Herzfeld, substituting, however, in his formula 0.062 for 0.05 for the increment of the factor. The reason for this difference in the factor of the two methods is due entirely to the amount of acid used in inversion.

It has been shown by a number of chemists that hydrochloric acid increases the specific rotatory power of levulose. Weber, at the ninth annual meeting of this association, reported that hydrochloric acid increased the reading of a solution of invert sugar, and that this increase varied with the amount of acid. Lippmann[c] gives the following table, showing the effect of different amounts of acid:

TABLE I.—*Effect of different amounts of hydrochloric acid on polarization of invert sugars.*

Weight of sugar.	Polarization, °Ventzke.			
Grams.	*5 cc HCl.*	*10 cc HCl.*	*15 cc HCl.*	*20 cc HCl.*
26.048.....	−34.00	−35.04	−35.95	−36.80
13.024.....	−33.00	−34.12	−35.15	−36.03

Lippmann's polarizations were all made at 20° C., and in the case of the half-normal weight the reading was multiplied by 2 for comparison. This table shows that hydrochloric acid, by its simple presence, affects the polarization.

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[a] Ztsch. Rub. Zuck. Ind., **40**: 898 (1890).
[b] Ztch. Rub. Zuck. Ind., **40**: 194 (1890).
[c] Chemie die Zucherartin, p. 800.

In Table II are some results of my own, showing that the addition of acid in the cold had the same effect as when it was used in the process of inversion:

TABLE II.—*Effect of different amounts of hydrochloric acid on polarization of invert sugars when added in the cold.*

Description of sample.	Polarization.	Temperature.	Change in rotation.
	° *Ventzke.*	°*C.*	
No. 1, containing no HCl	−23.0	18.0	.....
No. 2, containing 5 cc HCl, 67° C	−24.2	18.4	1.2
No. 3, containing 10 cc HCl, 67° C	−25.0	17.8	2.0
No. 4, containing 5 cc HCl (cold)	−24.2	18.4	1.2
No. 5, containing 10 cc HCl (cold)	−25.0	18.0	2.0
No. 6, containing 10 cc HCl (N/4) (cold)	−23.4	18.0	0.4

Table I also shows the different effects of equal amounts of acid on different weights of sugar. This is further shown in fig. 2, which illustrates the action of 10 cc of acid in 110 cc of sugar solutions of varying degrees of concentration.

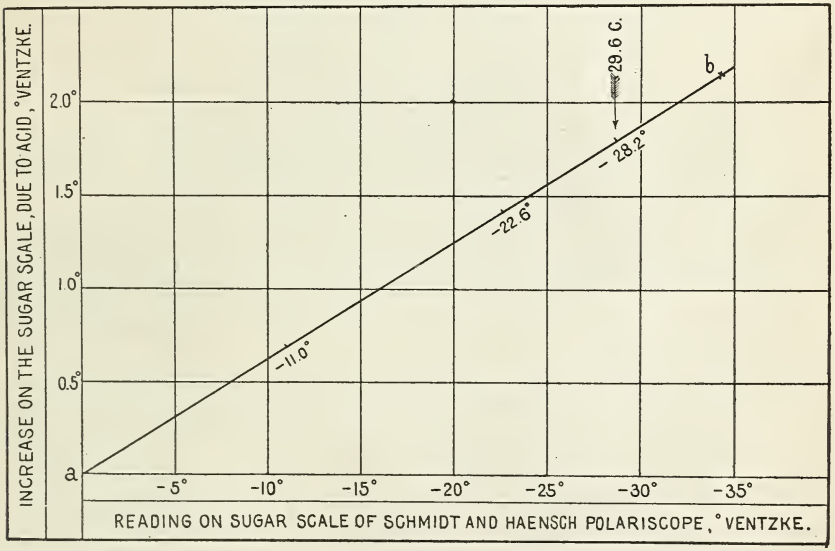

FIG. 2.—Effect of 10 cc of hydrochloric acid on 110 cc of sugar solutions of varying concentration.

To obtain this diagram (fig. 2) solutions of invert sugar of varying strengths were prepared and 10 cc of acid were added to 110 cc of the solution. The difference between the reading of the solution before and after the addition of the 10 cc of acid would give a point on the line a–b. The diagram also shows the effect due to concentration of the solution plus the effect due to the acid.

This work demonstrates that the factor for the Clerget or any other formula is a variable and that the amount of the variation depends on both the amount of acid and the amount of sugar used. The smaller the amount of acid, the more nearly the factor approaches a constant. These two facts, combined with the consideration that the factor for the German method has been carefully determined and that all the investigations of late years have been conducted according to this method, emphasize the wisdom of its adoption as the most accurate method now available.

At the suggestion of Dr. Spencer, the associate referee made some investigations as to the inversion of sugars at ordinary temperatures. This would have several advantages over the methods now employed. First, there would be no danger of the destruction of levulose as occurs from overheating. Further, when a large volume of work is being carried on it would be convenient to set the solutions aside and allow them to invert while other work is being done.

Hammerschmidt [a] worked out the time necessary for the complete inversion of 13.024 grams of sugar at different temperatures and with varying amounts of hydrochloric acid. The following table shows his results for temperatures ordinarily prevailing in the laboratory:

TABLE III.—*Time necessary to invert 13.028 grams sucrose dissolved in 100 cc (Hammerschmidt).*

Temperature.	5 cc HC.[a]	10 cc HC.[a]
°C.	*Hours.*	*Hours.*
10	225.0	94.0
15	101.0	44.0
20	47.0	20.0
25	23.0	10.0
30	11.6	5.0

[a] Specific gravity, 1.18.

From these figures it will be seen that with a temperature of 25° C. and 10 cc of hydrochloric acid to 100 cc, complete inversion takes place in 10 hours. Bornträger [b] showed that complete inversion could be brought about at from 20° to 23° C. by standing from eighteen to twenty hours.

The associate referee has made a number of tests of this method, conducting the work along the lines of the German official method. To a solution of 13.024 grams sucrose, 50 cc water and 5 cc hydrochloric acid (sp. gr. 1.18) were added. The solution was made up to 100 cc, placed in a 200-mm tube and the reading made. The results were as follows:

TABLE IV.—*Process of inversion during twenty-four hours (German official method).*

Time.	Polarization.	Temperature.	Time.	Polarization.	Temperature.
	°*Ventzke.*	°*C.*		°*Ventzke.*	°*C.*
11 a. m.	+50.0	25.8	3.10 p. m	− 7.20	25.8
12.40 p. m.	+10.0	25.8	3.30 p. m	− 8.20	26.0
12.44 p. m.	+ 9.50	25.8	3.57 p. m	− 9.50	26.0
12.55 p. m.	+ 7.60	25.8	4.24 p. m	−10.60	26.5
1.15 p. m.	+ 4.60	25.8	5 p. m	−11.65	27.3
1.34 p. m.	+ 2.00	25.8	8 p. m	−14.30	27.0
1.48 p. m.	.30	25.8	11.45 p. m	−14.85	26.4
2 p. m.	− 1.50	25.8	9.05 a. m.	−15.30	25.0
2.32 p. m.	− 4.30	25.8			

[a] Ztsch. Rub. Zuck. Ind. **40:** 465 (1890).
[b] Ztschr. Rub. Zuck. Ind. **40:** 881 (1890).

Bornträger[a] obtained very similar results at a temperature from 20 to 22° C. In order to determine whether the factor used in the German official method would be correct for this method of inversion, a number of comparative determinations were made on the same sugar, using both methods. The results are shown in the following table:

TABLE V.—*Comparison of inversion in the cold and by the German official method (half normal weight).*[a]

INVERSION IN THE COLD.

Polarization.	Temperature.	Cor. to 20° C. (×2).	Sodium acetate added.
° *Ventzke.*	°*C.*	° *Ventzke.*	*Grams.*
−15.28	24.5	−32.81	.....
−15.32	24.6	−32.94	.....
−15.27	24.7	−32.89	.....
−14.65	27.1	−32.85	1
−14.60	27.1	−32.75	3
−14.56	27.2	−32.75	.....
−14.68	26.8	−32.76	2
−15.50	23.6	−32.80	2
−15.38	23.6	−32.56	4

GERMAN OFFICIAL METHOD.

−15.90	22.05	[b] −32.83	.....
−15.78	22.65	[b] −32.89	.....
−15.70	22.95	[b] −32.88	.....

[a] Five cc hydrochloric acid (sp. gr. 1.18) were added to each solution which stood twenty hours at a temperature of 20° C.

[b] Average, −32.86 = 142.86 factor.

These solutions were polarized in a 400-mm tube to decrease the error of reading, and at exactly the same temperature the average of the factors calculated from inversion in the cold was 142.88, and by inversion by the German official method, 142.86, which shows a very satisfactory agreement between the two methods.

From the table it will also be seen that the presence of considerable amounts of sodium acetate does not interfere with the inversion, although it probably reduces the invert polarization, as is shown from the factor 142.85 when 1 gram of sodium acetate is present and 142.56 when 4 grams are present. Herles[b] showed that an addition of 3.4 grams sodium acetate reduced the reading of an invert sugar solution, inverted with hydrochloric acid, from −33.02° to −32.86.°

[a] Ztschr. Rub. Zuck. Ind. **40:** 881 (1890).

[b] Ztschr. Rub. Zuck. Ind. **40:** 220 (1890).

When the normal weight of sugar (26.048 grams) was used, the comparative inversions showed practically the same agreement, as can be seen from the following table:

TABLE VI.—*Comparative inversions made in the cold and by the German official method (normal weight).*[a]

INVERSION IN THE COLD.

Polarization.	Temperature.	Cor. 20° C.	Citric acid added.
° *Ventzke.*	°*C.*	° *Ventzke.*	*Grams.*
—30.73	26.2	—33.83	.....
—30.78	26.2	—33.88	.....
—30.83	26.1	—33.96	.....
—30.78	26.1	—33.83	.....
—30.78	25.9	—33.63	.....
—30.75	25.9	—33.60	2
—32.30	23.0	—33.80	2

GERMAN OFFICIAL METHOD.

—32.85	22.4	[b]34.00	.....
—32.32	23.2	[b]33.92	.....
—32.27	23.4	[b]33.97	.....

[a] Five cc hydrochloric acid (sp. gr. 1.18) were added to each solution which stood from twenty to twenty-four hours at a temperature of 26° C.

[b] Average, —33.96.

The factor as calculated from inversion in the cold is 143.86 and from inversion by heating 143.96. The method employed was to dissolve 13.024 or 26.048 grams in a 50-cc solution, add 5 cc hydrochloric acid, allow to stand at room temperature from twenty to twenty-three hours, make up to 100 cc, and polarize. This method requires that the temperature shall be above 20° C., as can be seen from Table III (Hammerschmidt). At lower temperatures the time of inversion is too long. At a temperature of 20° to 24° C., following the method as given above, the complete inversion of 13.024 grams of sugar will take place in from ten to twenty hours; at 25° it only takes ten hours. In many localities this is the temperature of the laboratory for most of the year, and it can be easily obtained in any laboratory.

Following Clerget's method as to the amount of acid and inverting in the cold with the normal weight of sugar (26.000 grams to 100 true cc) a polarization of —33.99° at 20° C. was obtained. When 10 cc of hydrochloric acid were added to 100 cc with the normal weight of sugar, and inversion was effected by standing twenty to twenty-four hours at 26° C., the polarization was —34.23° at 20° C. The addition of 2 grams of citric acid did not affect the reading.

In many kinds of work it would be a decided advantage to have an inverting agent which did not affect the specific rotatory power of the levulose. This is seen in the polarization of honey and the estimation of sucrose by inversion as set forth in the following table on the polarization of honeys:[a]

[a] U. S. Dept. of Agr., Division of Chemistry Bul. 13, Pt. 6.

TABLE VII.—*Polarization of honeys.*

Direct.	Invert.	° Ventzke.	
		Cane sugar.	Calculated invert reading.
−20.00	−20.90	0.72	−21.25
−17.60	−18.32	.93	−18.59
−16.8	−18.40	1.23	−18.20
−15.8	−17.5	1.31	−16.78
−11.0	−12.0	.....	−11.68
−13.2	−15.6	.....	−14.00
−16.50	−18.00	.....	−17.52
−14.80	−15.60	.....	−15.70
− 9.40	−10.67	.96	− 9.98
−12.90	−13.86	.73	−13.70
−14.40	−15.40	.76	−15.39
−11.30	−12.65	.99	−12.00
−11.50	−12.65	.85	−12.21
−13.50	−14.00	.30	−14.33
− 9.5	−10.00	.30	−10.05
−11.0	−12.00	.70	−11.68
−10.0	−11.00	.70	−10.62
−11.0	−12.00	.70	−11.68

By the ordinary method of inversion all of the samples appeared to contain cane sugar; but when the change in polarization, due to the addition of the acid, is calculated, as is shown in the fourth column, it can be seen that a considerable number contained no cane sugar whatever.

If an inverting agent could have been used which did not increase the specific rotatory power of levulose there would have been no change in polarization after inversion. Of course this difference can be calculated by the formula

$$S=\frac{(A-(B-.062B))}{141.85-\frac{T}{2}}.$$

If A equals (B−.062B), then the change in polarization is due to the acid added in inverting; but this formula only holds good for invert sugar. The presence of glucose renders such a calculation impossible, but it does not prevent a change in polarization, as is shown by the following data:

TABLE VIII.—*Effect of acid on invert sugar in the presence of glucose.*

Solution.	Polarized.	Temperature.
	° Ventzke.	*° C.*
13.028 grams invert sugar + 25 cc glucose solution	+9.8	21.0
The same + 10 cc hydrochloric acid	+8.9	21.0
The same + 5 cc hydrochloric acid	+9.4	21.0

Thus it is seen that when glucose which contains invert sugar is polarized before and after inversion, there will be a change of polarization even if there is no sucrose present. This condition would be almost always found in honey adulterated with glucose. This error could be prevented by the use of an inverting agent which did not affect the rotatory power of the levulose.

Weber[a] showed that in invert sugar prepared by inversion with acetic acid, the specific rotatory power of the levulose was the same as that of pure levulose, demonstrating that it had no effect on the specific rotatory power; but as acetic acid is a very weak inverting agent, citric acid being about three times as strong, the latter

[a] Jour. Am. Chem. Soc., 17: 321.

was tried. The strength used in all cases was 2 grams to 100 cc, and the time of heating thirty minutes at the temperature of boiling water. No destruction of invert sugar takes place under these conditions. The following table shows the results obtained by this method:

TABLE IX.—*Inversion by citric acid.*

Weight of sugar.	Polarization.	Temperature.	Polarization (Cor. to 0° C.).	Remarks.
	°*Ventzke.*	°*C.*	°*Ventzke.*	
Normal	−28.95	26.1	−42.00	Average −41.95.
Do	−28.89	26.0	−41.89	
Do	−28.97	26.0	−41.97	
Do	−29.00	26.0	−42.05	
One-half normal	−28.25	26.3	−41.39	Polarized in 400 mm tube −41.49 average.
Do	−28.27	26.4	−41.47	
Do	−28.27	26.5	−41.53	
Do	−28.17	26.6	−41.47	
Do	−29.40	26.7	−42.75	5 cc of hydrochloric acid (sp. gr. 1.186) were added before these were made up to volume; average −42.78.
Do	−29.29	26.9	−42.76	
Do	−29.35	26.9	−42.80	
Do	−29.35	26.8	−42.75	
Do	+40.30	23.3	.....	2 grams of sodium acetate were added with the citric acid, and practically prevented inversion.

From these results it can be seen that there is a small difference between the factor for normal weight and one-half normal weight, i. e., 141.95 and 141.49. This change in factor can be corrected by adding 5 cc hydrochloric acid before polarization, and the factor for the German method, 142.66, can be used, as will be seen from the results obtained when this method was followed. It will be noted, however, that sodium acetate greatly interferes with the hydrolysis and in fact almost stops it. This makes the use of citric acid practically of no value in solutions that have to be cleared with lead acetate, which of course greatly limits the value of the method, but in such substances as contain large amounts of invert sugar and small amounts of cane and do not have to be cleared with lead acetate this method will give very accurate results.

In a great many cases it is necessary to estimate cane sugar in the presence of maltose and dextrin. The following table shows the effect of the different methods of inversion on a glucose sirup containing a very high per cent of maltose and dextrin. In all cases the inversion by standing over night, twenty hours, shows less effect than the German official method, or the inversion with citric acid, boiling half an hour.

TABLE X.—*Effect of inversion on glucoses rich in maltose and dextrin.*

POLARIZATION OF SOLUTION MODIFIED AS INDICATED.

Description of sample.	Original solution.	(1) +5 cc HCl at 68° C.	(2) +5 cc HCl 20 hours in cold.	(3) +2 grams citric acid; one-half hour, 100° C.	Decrease in polarization.		
					(1)	(2)	(3)
	°*Ventzke.*	°*Ventzke.*	°*Ventzke.*	°*Ventzke.*	°*Ventzke.*	°*Ventzke.*	°*Ventzke.*
	+56.20	+55.87	+55.95	.....	−0.33	−0.25	.....
	+36.66	.....	.....	+36.12	.....	.....	−0.54
	+36.69	+36.40	+36.64	+36.28	− .29	− .05	− .41
XXX	+47.15	.....	+46.95	+46.78	.....	− .20	− .37
XX	+42.12	.....	+41.82	+41.74	.....	− .30	− .38
XXXX	+46.12	.....	+45.75	+45.60	.....	− .37	− .52

The PRESIDENT. If there are no other papers on sugar, I will call for the report of the referee on tannin.

REPORT ON TANNIN.

By WM. H. TEAS, *Referee.*

For this year's experimental work the following samples were sent to 18 chemists: Chestnut extract, quebracho extract, and a union liquor.

The work on the extracts consisted in a comparison of results on soluble solids obtained by the use of single and double filter paper (S and S 590). Analyses were made according to the official method, the optional use of any good grade of filter paper for nontannin filtration being the only change.

DOUBLE AND SINGLE FILTERS.

The question of the comparative influence of different amounts of filter paper in contact with tannin solutions upon the results on soluble solids led to these experiments. It is understood that the filter paper does absorb tanning matter, and this being the case, it is argued that the least amount of paper essential to a clear filtrate should come in contact with the solution. Mr. H. C. Reed undertook some experiments along these lines which are more complete than circumstances will permit reporting in detail. His results as regards filter paper known as 590 S and S were as follows:

Results on soluble solids with single filter for fourteen tanning solutions, ranging from a clear solution of a tanning extract to quebracho solutions, showed an average increase of 0.47 per cent over the results secured on the same solutions by the use of double filters; the official method was used in all cases.

The results of the work on this year's samples show an increase in soluble solids where the single filter was used over the average of double filter results on soluble solids, of 0.23 per cent in the case of the chestnut extract, and an increase of 0.74 per cent on the quebracho extract. This, too, despite the fact that the analyses were made by different chemists and the evaporation and drying took place under different conditions. In general the individual results bear out the indications of the average, there being but two results (both on chestnut extract) in which the soluble solids with double paper exceeded results from single paper. The single filter method requires a longer time for filtration and there is a possible chance of error here, unless all possible precautions against evaporation are taken.

On the question of double or single filter paper, some of the collaborators have expressed themselves as follows:

Mr. Wilson says: "I am convinced that 590 S and S single with assistance will trap all insolubles, and it is certainly desirable to have the least possible amount of paper in contact with a tannin solution. The difference is not so great in quick filtering solutions like chestnut, but on slow filtering solutions, rich in insolubles, the difference is marked, which should, we think, bring the 590 single strongly into favor."

Mr. Reed favors the single paper.

Mr. Alsop is of the opinion that single paper will remove all insolubles.

Mr. Alden says: "I hope the double filter will be retained, for there seems to be a considerable difference in the case of quebracho. The filtrate was not clear, as in the case of the double filter."

Turbid filtrates have caused the referee to hesitate to recomend the adoption of the single paper; with the double paper, kaolin, and ordinary care, a clear quebracho filtrate can always be secured. Single paper has not always given clear filtrates and sometimes necessitates two or three trials. If the single filter gives as clear a filtrate as the double, then there can be no question as to the correctness of the higher soluble solids results obtained from the single filter. It is only with unclarified quebracho and similar extracts that the annoyance of turbid filtrates occurs; and

as it is questionable whether the analysis of such extracts represent their true value in the tannery—because of the dissolving temperature, and strength at which they are used differing greatly from the conditions in the laboratory—it is extremely important that every particle of insoluble matter be determined.

Apropos of this matter, I desire to quote from Mr. Alsop's report to the referee: "I regret to say that I did not notice that you said to take 10 grams quebracho to the liter. I took 25.32 grams for 2 liters, which, while it falls within the limits prescribed by the method, will probably make my results low in tannin." This statement indicates a condition of affairs which is patent to every chemist who has had any experience with the analysis and use of extracts rich in insolubles.

With the advantages and disadvantages of the single filter paper in mind, I advocate its trial for determinations of soluble solids, provided that all dryings shall be made from perfectly clear filtrates.

Acid Determinations.

Acid determinations by three methods were made on the union liquor sent out. I may here remark that formaldehyde was used on the liquor to keep the initial amount of acid constant. The distillation method directions were as follows:

Take 125 cc of original liquor, distill over 100 cc, and titrate distillate with phenolphthalein and N/10 sodium hydrate. Call this result 80 per cent of total volatile acid in the liquor (i. e., 80 per cent of acid in 100 cc of original liquor).

This method was formerly in use in the laboratories of the United States Leather Company, the procedure of calling the acid in the first 100 cc, 80 per cent of the acid in 100 cc of the liquor having been determined on, after a series of experiments made some years ago. The standard method for comparison used in these experiments I am unable to give, as the data are not now at hand. It has been regarded as a fair comparative method for the volatile acid determination in tan liquors, the low results having been attributed to the percentage of lactic acid in the liquor, which results from this method would not show.

At the suggestion of the referee, Mr. H. C. Reed made some experiments on the determination of acid in acetic and lactic acid solutions of known strength by the three methods indicated by the referee. In these experiments commercial grades of acid were used; 125 cc of acetic and lactic acid solutions and 125 cc of a solution of the two combined, in the ratio of 50 per cent each, were distilled to 100 cc distillate, and the distillates titrated with N/10 sodium hydrate. The following results were obtained:

Acetic acid solution containing 0.664 per cent showed 0.69 per cent.
Lactic acid solution containing 0.58 per cent (as acetic) showed 0.019 per cent.
Acetic and lactic (equal parts) containing 0.623 per cent (as acetic) showed 0.371 per cent.

Experiments conducted on the same lines, but with chemically pure acids, gave the referee the following results:

Acetic solution containing 0.84 per cent showed 0.44 per cent.
Lactic solution containing 0.88 per cent showed 0.011 per cent.
Acetic and lactic solution containing 0.86 per cent showed 0.22 per cent.

Acid determinations made by any distillation method can not include the lactic acid content, as it can not be distilled unchanged, but is broken up by heat into lactic acid, and ultimately into lactide. Distillation methods involving the distilling over of nearly all the original liquor subject the acid to the danger of decomposition by the greater heat of the parts of the still not covered by the residue.

Of the distillation methods used in this year's experiments, Mr. Wilson writes: "The chief objection to the distillation method is in assuming the 100 cc of distillate to contain only 80 per cent of the total acid in the liquor, although the results so obtained seem to bear out the assumption."

Determinations by the Kohnstein-Simand method were made by heating 100

cc of the original tan liquor with 3 to 4 grams of freshly ignited chemically pure magnesia, filtering, removing lime, and determining gravimetrically the magnesia in the filtrate. Theoretically this is probably the best method, but it is too tedious and requires too much care and time to be of practical use in a laboratory where many acid determinations are made. The filtration of the liquor is slow, and, in the case of many heavy liquors from acid hemlock tanneries, it is impossible unless the funnel is kept hot by means of a hot-water jacket.

Mr. Reed reports: "Determinations were made (Kohnstein-Simand method) in triplicate upon solutions of acetic and lactic acids and a combination of the two, in the ratio of 50 per cent each, with the following results:

"Acetic acid solution 0.663 per cent by titration showed 0.664 per cent.

"Lactic acid solution 0.536 per cent by titration showed 0.581 per cent.

"Acetic and lactic acid solution 0.579 per cent by titration showed 0.623 per cent.

"The method does not permit of very rapid determinations, and even if it gives more accurate results, which is doubtful, the writer believes it should be discarded for this reason."

Mr. Wilson says: "The magnesia method might be, when properly handled, the most accurate of the methods under consideration. It has the objection, however, of being tedious, and is open to sources of error in manipulation."

For the charcoal methods 100 cc of the original liquor were diluted to 500 cc and the diluted solution was used for the methods (*a*) and (*b*):

(*a*) To 100 cc of the diluted liquor add 2½ grains of animal charcoal, stir thoroughly every fifteen minutes for two hours, throw on filter and titrate an aliquot portion of the clear filtrate with N/10 sodium hydrate, after the addition of about 200 cc of distilled water.

(*b*) To 100 cc of diluted liquor add 2½ grains charcoal, bring to boiling point with constant stirring, filter, and titrate.

For comparable results by the charcoal methods it is essential that the animal charcoal shall be free from acids and carbonates; the charcoal sent out with the samples is an imported product and has given even results for some six months past.

Results by these methods are generally lower than the actual acid content, but the difference with every lot of charcoal of the best grade is constant, and if a correction for this difference be made the result is nearly absolute.

The objection to method (*a*) seems to be to the length of time the charcoal is in contact with the liquor; results from method (*a*) are invariably lower than those obtained from method (*b*). The difference, however, is not due entirely to the time of contact, but to some extent to the decreased volume of liquor caused by evaporation while heating. Mr. Reed reports on his experiments with acid solutions with these methods as follows:

Two samples of charcoal were used in these experiments, one furnished by the referee and the other an impure grade purified by treatment with hydrochloric acid and washing. Methods (*a*) and (*b*) were used, the latter modified by using a flask with tube condenser and frequent shaking. Charcoal from referee is marked (*c*) and that prepared by writer (*d*):

TABLE I.—*Comparative results obtained with two charcoals.*

Volume of solution.	Acetic acid solution.		Lactic acid solution.		Combination (50 per cent acetic, 50 per cent lactic).	
	(c)	(d)	(c)	(d)	(c)	(d)
40 cc solution required without treatment N/10 NaOH	cc 8.85	cc 8.85	cc 7.75	cc 7.75	cc 8.30	cc 8.30
40 cc solution required by method (*a*) N/10 NaOH	6.95	7.70	5.3	7.55	5.90	7.65
40 cc solution required by method (*b*) N/10 NaOH	7.1	7.95	5.35	7.65	5.95	7.80

It will be noted that charcoal purified by the writer gave almost theoretical results in the case of the lactic acid solution, but with the acetic acid solution considerable loss of acid resulted. By treatment of the acetic acid solution with various amounts of a charcoal and calculation of the loss of acid from a given weight of charcoal, practically theoretical results were obtained.

The referee's experiment along the same lines with the same charcoal as that sent out resulted as follows:

TABLE II.—*Comparison of two charcoal methods.*

Volume of solution.	Acetic acid.	Lactic acid.	Acetic and lactic.
	cc	*cc*	*cc*
40 cc solution required without treatment, N/10 NaOH	10.8	10.2	11.4
40 cc solution required by method (*a*) N/10 NaOH	9.4	8.8	9.9
	9.4	8.8	9.8
	9.35	8.8	9.9
	9.4	.....	.....
40 cc solution required by method (*b*) N/10 NaOH	9.9	9.15	10.1
	9.9	.....	.....

The use of purified bone black was suggested in the instructions in making determinations by this method, the process consisting of treatment with dilute hydrochloric acid, subsequent washing and drying, and a final heating almost to the point of combustion. Mr. Reed's results with charcoal treated in this manner are given above. The referee heated some charcoal similar to that accompanying the samples and on the liquor sample made the following determinations: By method (*a*), 0.40 and 0.40 per cent; by method (*b*), 0.42 and 0.415 per cent.

From the table given on the determination of acid by the three methods, the Kohnstein-Simand method seems to give the least concordant results. As stated above, the slow filtration and the number of distinct operations necessary seem to afford too many opportunities for error.

The distillation method as used in this work depends too much on the 80 per cent hypothesis. In this case the results are close to those from the charcoal methods, but it has been the referee's experience that many liquors showing a certain percentage of acid by the distillation method will give almost double when treated with charcoal.

It seems to be the opinion of the majority of the collaborators that the charcoal methods are sufficiently accurate and comparable for adoption. The following comments were made on this point:

Mr. Wilson.—It seems to the writer that the simple charcoal method is sufficiently accurate for the control of yard liquors.

Mr. Reed.—The writer is inclined to the charcoal methods for the determination of total acids, preferring method (*b*) with the variation of a flask and tube condenser.

Mr. Small, differing from these views, writes: "The methods outlined (Kohnstein-Simand excepted) introduce such large errors in the amount of acid contained, by reason of the treatment necessary to get clear liquors, that they are valueless save for comparison." He advocates the acid method in which the tannin is precipitated by gelatin and the resulting liquid titrated, using spot test with litmus for end reaction.

TABLE III.—*Results of experiments with chestnut extract, using single S. and S. 590 filter paper.*

Analyst.	Moisture.	Total solids.	Soluble solids.	Reds.	Nontannins.	Tannins.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
F. P. Veitch	.....	43.48	42.93	0.55	17.92	25.01
J. H. Yocum	56.15	43.84	43.52	.33	19.22	24.30
F. H. Small	56.40	43.36	42.40	.96	17.43	24.97
C. H. Brown	55.61	43.94	43.23	.71	17.20	26.03
W. K. Alsop	.....	43.72	43.18	.54	17.46	25.72
Frederick Alden	.....	43.35	42.80	.55	18.42	24.38
H. T. Wilson	56.17	43.48	[a]42.51	1.02	.....	25.78
	56.15	43.53	42.34	1.19	16.73	25.61
H. C. Reed	.....	43.76	43.18	.58	17.57	25.61
C. C. Hildebrand	.....	43.33	42.88	.45	17.23	25.65
W. H. Teas	.....	43.43	42.43	1.00	16.92	25.51
		43.32	42.36	.96	16.89	25.47

[a] Laboratory paper.

	Per cent.
Average soluble solids	42.81
Lowest soluble solids	42.34
Highest soluble solids	43.52
Greatest difference from average	.71

TABLE IV.—*Results of experiments with chestnut extract, using double S. and S. 590 filter paper.*

Analyst.	Moisture.	Total solids.	Soluble solids.	Reds.	Nontannins.	Tannins.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
F. P. Veitch	.....	43.48	42.62	0.86	17.92	24.70
W. H. Krug	.....	43.04	41.52	1.52	15.80	[a]25.72
J. H. Yocum	56.15	43.85	43.74	.12	19.22	24.51
F. H. Small	56.40	43.32	42.29	1.03	17.49	24.80
C. H. Brown	55.61	43.94	43.00	.94	17.20	25.80
W. K. Alsop	.....	43.72	43.07	.65	17.46	25.61
Frederick Alden	.....	43.51	43.03	.48	18.60	24.43
H. T. Wilson	56.17	43.48	[b]42.26	1.22	16.73	25.53
	56.15	43.53	42.33	1.15	16.73	25.60
H. C. Reed	.....	43.76	42.91	.85	17.57	25.34
C. C. Hildebrand	.....	43.33	42.25	1.08	17.23	25.02
W. H. Teas	.....	43.43	42.32	1.11	16.92	25.40
		43.32	42.21	1.11	16.89	25.32

[a] Dried five hours in vacuo, at 100° C. [b] Laboratory paper.

	Per cent.
Average soluble solids	42.58
Lowest soluble solids	41.52
Highest soluble solids	43.74
Greatest difference from average	1.16

TABLE V.—*Results of experiments with quebracho extract, using single S. and S. 590 filter paper.*

Analyst.	Moisture.	Total solids.	Soluble solids.	Reds.	Nontannins.	Tannins.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
H. T. Wilson	52.49	.....	[a]43.02	4.52	.....	35.98
	52.44	47.54	43.08	4.46	7.04	36.04
F. P. Veitch	.....	48.00	43.68	4.32	7.07	36.61
J. H. Yocum	52.39	47.61	43.28	4.33	9.06	34.22
F. H. Small	52.42	47.10	42.72	4.38	7.25	35.47
C. H. Brown	52.22	47.69	43.28	4.41	7.42	35.86
W. K. Alsop	.....	47.41	42.46	4.95	7.56	[b]34.90
Frederick Alden	.....	48.03	45.35	2.68	7.39	37.96
H. C. Reed	52.50	47.47	43.39	4.08	7.13	36.26
Harry Gerber	52.13	48.72	46.23	2.49	7.31	[c]38.92
C. C. Hildebrand	.....	47.68	43.54	4.14	7.81	35.73
W. H. Teas	.....	47.46	44.32	3.14	7.43	36.89
		47.45	44.46	2.99	7.47	36.99

[a] Laboratory paper. [b] Twelve and one-half grams extract to liter. [c] Fifty cc evaporation.

	Per cent.
Average soluble solids	43.75
Lowest soluble solids	42.46
Highest soluble solids	46.23
Greatest difference from average	2.48

TABLE VI.—*Results of experiments with quebracho extract, using double S. and S. 590 filter paper.*

Analyst.	Moisture.	Total solids.	Soluble solids.	Reds.	Non-tannins.	Tannins.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
H. T. Wilson	52.49	.....	[a]42.61	4.93	.....	35.57
	52.44	47.54	42.23	5.31	7.04	35.19
H. C. Reed	52.50	47.47	42.93	4.54	7.13	35.80
F. P. Veitch	.....	48.00	43.40	4.60	7.07	36.33
W. H. Krug	.....	48.23	42.20	6.03	6.93	[b]35.27
J. H. Yocum	52.39	47.61	43.00	4.61	9.06	33.94
F. H. Small	52.42	47.09	42.39	4.70	7.30	35.09
C. H. Brown	52.22	47.69	42.83	4.86	7.42	35.41
W. K. Alsop	.....	47.41	41.72	5.69	7.56	[c]34.16
Frederick Alden	.....	47.75	43.64	4.11	7.17	35.47
Harry Gerber	52.13	48.72	46.05	2.67	7.31	[d]38.74
C. C. Hildebrand	.....	47.68	43.16	4.52	7.81	35.35
W. H. Teas	.....	47.46	43.02	4.44	7.43	35.59
	.....	47.45	42.97	4.48	7.47	35.50

[a] Laboratory paper.
[b] Dried 5 hours in vacuo at 100° C.
[c] Twelve and one-half grams to liter.
[d] Fifty cc evaporation.

	Per cent.
Average soluble solids	43.01
Lowest soluble solids	41.72
Highest soluble solids	46.05
Greatest difference from average	3.04

TABLE VII.—*Comparison of results on soluble solids.*

Results compared.	Chestnut.		Quebracho.	
	Single paper.	Double paper.	Single paper.	Double paper.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
Average soluble solids	42.8	42.58	43.75	43.01
Lowest soluble solids	42.34	41.52	42.46	41.72
Highest soluble solids	43.52	43.74	46.23	46.05
Greatest difference from average	.71	1.16	2.48	3.04

TABLE VIII.—*Results with different methods of determining total acidity.*

Analyst.	Distillation.	Kohnstein-Simand.	Charcoal.	
			(a)	(b)
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
H. T. Wilson	0.355	0.350	0.397 .393	0.426 .420
H. C. Reed	.3945	.4458	.42	*a*.4725
F. P. Veitch	.38	.60	.41	.45
J. H. Yocum	.40	.44	.34	.35
F. H. Small	.36	.65	.40	.42
C. H. Brown	.37	.....	.37	.43
W. H. Alsop	.37	.48	.36	.42
Frederick Alden	.438	.....	*b*.44	.....
Harry Gerber	.37	.67	.39 .368	.44 .4125
C. C. Hildebrand	.352 .354	.....	.375 .38	.45 .409
W. H. Teas	.360	.53	.38	.416
J. H. Norton	.31	.73	.39	.46

a When condenser was used, the result was 0.42 per cent; with purified boneblack it was 0.4125.
b Three hours' contact.

RECOMMENDATIONS.

As the official method for total acid in tan liquors for this year, the referee proposes the following:

To 100 cc of diluted liquor in a flask with tube condenser add 2 grams chemically pure animal charcoal, bring to boil with frequent shaking, filter, cool, and titrate an aliquot portion.

The following provisional method is also proposed:

To 100 cc of diluted liquor add 2½ grams animal charcoal, stir every fifteen minutes for two hours, filter, take an aliquot part and titrate.

It is convenient to take 40 cc of the filtrate and titrate with N/10 sodium hydrate, as this amount is soon filtered and admits of rapid calculation.

It is highly imperative that the charcoal be free from acid and carbonates and preferable that it be recently freshened by careful heating. Treatment of impure charcoals with dilute acid, followed by ample washing and then heating, will result in a charcoal which will give good results.

The following modifications of the official method are recommended:

To omit the moisture determination.

To change (*b*) in paragraph III so as to read:

Evaporations shall take place under precisely the same conditions as to contact with steam or with a metallic plate. All dryings called for after evaporation shall be done

by one of the following methods, under precisely the same conditions, so that the different residues of each analysis may occupy the same shelves in the drying oven:

1. For eight hours at the temperature of boiling water in steam bath.
2. For six hours at 100° C. in air bath.
3. For five hours in vacuo at 100° C.

V. Soluble solids, to read as follows:

Single pleated filter paper (S. and S. 590, 51 cm.) shall be used. To 2 grams kaolin add 75 cc of the tannin solution, stir, let stand fifteen minutes and decant as much as possible (not on the filter); add 75 cc of the solution, stir, and pour on the filter; keep filter full, reject the first 150 cc of filtrate, evaporate and dry next 100 cc. The portion dried for determination shall be perfectly clear and evaporation during filtration must be guarded against.

VI. Nontannins: Two grams kaolin to be used when filtering.

Omit paragraph VIII on testing hide powder, and section (*b*) of paragraph IX.

For next year's work the referee recommends additional experimental work on soluble solids, acid determinations, and on the amount of extract taken for analysis.

The President. I understand that there is one more paper to be presented on tannin, but as Mr. Frear, chairman of the committee on food standards, is compelled to leave to-night, we will listen to his report now, if there is no objection.

REPORT OF THE COMMITTEE ON FOOD STANDARDS.

By Wm. Frear, *Chairman*.

Mr. President and Gentlemen: Your committee on food standards would respectfully report with reference to the work of formulation of definitions and standards for foods as follows:

The association has reason for congratulation upon the fact that the conservatism, earnestness, and efficiency of its work, which have won pleasant recognition of its public usefulness in the past, are given distinct recognition by Congress in the appropriation act of the last session for the Department of Agriculture. This act states that "The Secretary of Agriculture, in collaboration with the Association of Official Agricultural Chemists and such other experts as he may desire to consult, shall fix standards for all food products for the information and guidance of the officials and courts charged with the execution of pure-food laws."

During the past year a number of sets of definitions and standards have been revised and prepared for submission to the trade, members of the association charged with food control work, State dairy and food commissioners, and others, to serve as a basis for suggestion and criticism that may assist the committee in perfecting these definitions and standards so as to make them representative of the legitimate trade of to-day. For assistance in the distribution of these schedules the committee is under special obligations to the honorable Secretary of Agriculture and the chief of the Bureau of Chemistry.

Your committee has considered the suggestions from the trade, and has practically completed its work upon two schedules; and it hopes to have ready for submission by the end of the year sets of definitions and standards for the following principal classes of goods: Meat, milk, cereal products, salad oils, spices, wines, vinegars, malted liquors, tea, coffee, and cocoa products, relative to most of which correspondence is now in progress with the trade interests concerned.

In view of the authorization previously granted to this committee, enabling it to bring its work at given stages to completion during intervals between the meetings of the association, and of the desirability of accompanying the definitions and standards, when issued, with a full statement of the principles governing the committee in their formulation, it has been thought preferable not to present at this date the definitions and standards for the several schedules upon which the work of the committee has been practically completed.

It is respectfully requested that the committee be continued.

Mr. WILEY. I have just received a telegram from Dr. Smith, director of the Agricultural Experiment Station of Michigan, stating that Dr. Kedzie is seriously ill and his recovery is possible, but improbable.

On motion, the secretary was instructed to send a telegram of sympathy on behalf of the association.

[The following telegram was sent in accordance with these instructions: "The association sends cordial sympathy to Dr. Kedzie and earnest hopes for a speedy recovery."

Dr. Kedzie lingered until November 7, when his death took place at his home at Agricultural College. The following brief biography and the portrait which constitutes the frontispiece of this bulletin are given place as the last tribute of the association to the memory of one who had long been a valued and beloved coworker.—The Editor.]

A MEMOIR OF THE LATE R. C. KEDZIE.

By L. S. MUNSON.

Robert Clark Kedzie was born at Delhi, N. Y., January 28, 1823. At the age of 3 years he went with his parents to Michigan, where they settled in Lenawee County. They were among the pioneers of that section, and the father having died soon after settling in that region, it was left to the mother and seven children to make for themselves a home under these adverse circumstances. At the age of 17 Robert entered Oberlin College, and graduated six years later. Meanwhile he had supported himself largely by work outside of college duties and by teaching school during vacations. Immediately upon graduation he took charge of Rochester Academy, in Oakland County, which position he held for two years. He then entered the medical school of the University of Michigan, and in 1851 received the degree of M. D. with the first graduating class of that institution. After practicing medicine first at Kalamazoo for one year, and later at Vermontville for ten years, he enlisted with the Twelfth Michigan Infantry. He returned to Michigan in 1863, and was at once appointed professor of chemistry at the Michigan Agricultural College. This position he held until July 1, 1902, when he was relieved of active duties at his own request, and was made professor emeritus.

In 1863 Oberlin College bestowed upon Dr. Kedzie the degree of M. A. In 1898 the Michigan Agricultural College, in recognition of his long and valued service as a scientist, honored him with the degree of D. Sc., and in 1901 the University of Michigan conferred upon him the highest honor in its power, the degree of LL. D.

It was in his capacity as professor of chemistry at the Michigan Agricultural College that his work stands out most prominently. He became connected with that institution at a time when its fate was hanging in the balance; an agricultural college was a new institution and had to demonstrate its usefulness before the people of the State. While Dr. Kedzie had in his own mind no doubt as to the value of such an educational institution, the demonstration of its usefulness was a matter of extreme difficulty. In many cases sentiment was against the college. The legislature was hostile, and support was obtained with difficulty. It was against these odds that the authorities had to work, and to no other man is more credit due for the ultimate success of the institution than to Dr. Kedzie. Not only in its formative period, but in all its subsequent history, he was a dominating factor. A persistent worker, an untiring fighter when once he felt that he was in the right, and a man with conscientious regard for the welfare of the common people, he made his influence felt, not only at the college and throughout the State, but through these institutions he became a man of national reputation.

During his service of thirty-nine years at the college he gave instruction in chemistry to every class save two. He was a natural teacher, and had the faculty to a marked degree of infusing into his students the enthusiasm for his subject that he himself felt. There was no place in his class room for the idler, but for the student he always manifested a keen interest. His classes were always the most popular at the college. The work of the students was always of the first order, not because he compelled it, but because respect for the man commanded it.

In characterizing his services to science and to mankind, Dr. Victor C. Vaughn, of the University of Michigan, speaks as follows:

I know of no other man who has done so much for the betterment of human life. He was the first to investigate the dangers of arsenical wall papers and to inaugurate legislation looking to the discontinuance of their manufacture. He also investigated the dangers of inferior illuminating oils, and legislation safeguarding the people against them was enacted. Dr. Kedzie has justly been called the father of the beet-sugar industry in Michigan. He showed that something could be grown on the lands where the pine forests had been cut off. As a member of the State board of sanitation he was a leader. He accomplished things. The State of Louisiana, through his efforts, inaugurated a quarantine at New Orleans, the first of its kind in the world, and when Asiatic cholera appeared at the port of New York it was largely because of his influence that it was possible to say: "Thus far shalt thou come, and no farther."

Dr. Kedzie was one of the original members of the Michigan State board of health, and acted as its president for four years. He served as chemist of the experiment station from the time of its establishment in Michigan until his death, and it was largely through his efforts that the inspection of commercial fertilizers was established in the State. Twenty-five years ago he fought and won the battle for winter wheat that the millers were determined to grade below quality. He took an active interest in the work of the Association of Official Agricultural Chemists, and in 1898 he was elected president of the association.

Personally Dr. Kedzie was an exceptional man. His strong, vigorous mind, his frankness of manner, his forceful presentation of facts, his sympathetic and loving spirit won for him the kindest regard and the respect of all who knew him. He had those qualities that make a great man. He had to a remarkable degree the power of concentrating his mind upon a subject until he had completely mastered the facts; and he had the courage to assert what he believed, regardless of whose interests it affected. In the class room and out, the aim to get at the truth asserted itself and made its impression upon those with whom he came in contact. No student ever had a firmer friend than was Dr. Kedzie; no deserving student ever went to him in trouble without receiving some form of assistance.

Dr. Kedzie died November 7, 1902, after an exceedingly distressing illness of about six weeks. He was taken with an affection of the heart which made breathing difficult, yet, through all his suffering, the same invincible will power, the same heroic tenacity of purpose bore him up. Those who knew him personally feel his death as a great personal loss, and the loss of his influence will be severely felt by all who have been associated with him and especially by the institution with which he was so long connected.

Mr. Wiley. I move that the discussion of the report on food standards as well as the reports and discussion on tannin be postponed until to-morrow as we must now give up this room.

The motion prevailed.

On motion by Mr. Davidson the association adjourned at 4 p. m. until 9.30 Friday morning.

SECOND DAY.

FRIDAY—MORNING SESSION.

The meeting was called to order by the president at 9.30 a. m.

The PRESIDENT. The first report in order is that on the separation of nitrogenous bodies, by Mr. Van Slyke.

REPORT ON THE SEPARATION OF NITROGENOUS BODIES.

BY L. L. VAN SLYKE, *Referee.*

The referee decided to confine his work this year to the proteolytic products of milk and cheese in the hope of preparing methods of estimation which could be later subjected to critical examination at the hands of different analysts. The work covered by this report has been largely done in the laboratory of the New York Agricultural Experiment Station, at Geneva, by Mr. E. B. Hart. This report is more accurately entitled "Methods for the estimation of the proteolytic compounds contained in cheese and milk."

When milk-casein and its salts, or paracasein in cheese and its salts, are acted upon by dilute acids or alkalies under certain conditions, or by enzyms, or by micro-organisms, the proteid bodies are split up, forming a variety of complex cleavage products. The extent and intensity of such proteolytic changes are measured by the proportions and kinds of the different compounds resulting from the decomposition. In the ripening process that takes place in cheese, we have an instance of extensive proteolysis in the case of the nitrogen compounds of the fresh cheese, due probably to the combined action of dilute acid, enzyms, and micro-organisms. In our study of the causes that produce cheese-ripening and of the conditions that influence the process, we were, at the start, brought face to face with the difficulty involved in the lack of satisfactory methods for making quantitative separations and determinations of the products of cleavage formed. While we have well-elaborated methods for estimating the amount of casein and albumin in fresh milk, these are of little aid in studying the products of their decomposition. Little attention has been given to the development of methods that are applicable to the products occurring in this field. Serious difficulties are involved in such a study. First, we know at present only in an extremely meager and vague way the chemical constitution of milk-casein and and its allied compounds. As regards the constitution of the various compounds formed by the proteolysis of casein, we are largely in the dark, except in the case of some of the simpler ones. In the second place, this field is difficult to study, because the quantities of individual compounds that we have to work with are usually very small. Under these conditions, methods of quantitative separation must, at best, be regarded as largely empirical and more or less tentative. Instead of estimating individual compounds, about which our chemical knowledge is complete, we are compelled, in a large degree, to estimate groups of compounds, the individual members of which we know, for the most part, incompletely or not at all.

From the peptic digestion of casein, Chittenden has separated the proto- and deutero-caseoses,[a] and from a tryptic digestion, a deutero-caseose and a peptone.[b]

[a] Studies in Physiol. Chem., Yale Univ., **2**: 156 (1884–85).

[b] Studies in Physiol. Chem., Yale Univ., **3**: 66 (1887–88).

Alexander[a] has separated hetero-caseose from a peptic digestion of casein, but only in small quantities. Many investigators have observed paranuclein or pseudonuclein, the insoluble residue remaining from the peptic digestion of casein or paracasein. Emil Fischer and P. A. Lavene[b] have obtained pyrrolidin-α-carbonic acid from a tryptic digestion of casein.

By hydrolysis of casein with hydrochloric acid, Cohn[c] obtained 1-parahydroxyphenyl-α-amidopropionic acid (tyrosin), 1-α-amido-isobutylacetic acid (leucin), amidosuccinic (aspartic) acid, α-amidoglutaric (glutamic) acid, a pyridin derivative, and ammonia; by the same means, Emil Fischer[d] has recently isolated, among the monoamido acids, in addition to products previously obtained by others, amidovaleric acid, phenyl-α-amidopropionic acid (phenylalanine), pyrrolidin-α-carbonic acid, and probably amido-acetic acid (glycocoll).

Among the crystallizable end products which have been found in ripening cheese are the following: Tyrosin, leucin, histidin, α-ε-diamidocaproic acid (lysin), tetramethylenediamine (putrescin), pentamethylenediamine (cadaverin), lysatin, guanidin probably, and ammonia. Most of these products have been recently reported by Winterstein and Thöny[e] as being found in Emmenthaler cheese. Excepting cadaverin and guanidin, they had also been previously found, though not reported, in American cheddar cheese in this laboratory. It is very probable that other amido compounds will be found, sooner or later, among the products formed by the tryptic, if not the peptic, digestion of milk-casein and of cheddar cheese.

In cheese we find, earlier or later, during the ripening process, a series of compounds and groups of compounds, which, so far as we know at present, appear in something like the following order of succession: (1) Paracasein, (2) unsaturated paracasein lactate, (3) paranuclein (pseudonuclein), (4) caseoses (albumoses), (5) peptones, (6) amido-acid compounds, and (7) ammonia. After the early stages of ripening we have present at the same time all these different compounds and groups.

We shall consider methods for the separation and estimation of the proteolytic products found, first in cheese, and second in milk, following the general order indicated above. It may be well to say at the outset that in dealing with the separation of nitrogenous bodies so complex in composition as those mentioned above and occurring in very variable quantities, we can hope at present in the study of milk and cheese problems only to approximate accurate quantitative results. While we have in the Nencki method a very accurate means of estimating ammonia, the methods used in separating peptones from amido compounds can not be relied upon to give us more than approximate results.

I. Methods for the Separation and Estimation of the Nitrogen Compounds of Cheese.

The description and discussion of the methods used for the separation and estimation of the nitrogen compounds of cheese will be presented in the following order:

1. Obtaining sample.
2. Determination of total nitrogen in cheese.
3. Extraction of water-soluble products.
4. Determination of total water-soluble nitrogen.
5. Determination of nitrogen in the form of paranuclein.

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[a] Zeit. f. Physiol. Chem., **25**: 411 (1898).
[b] Zeit. f. Physiol. Chem., **33**: 170 (1901).
[c] Ber. deut. Chem. Ges., **29**: 1785 (1896).
[d] Zeit. f. Physiol. Chem., **33**: 151 (1901).
[e] Zeit. f. Physiol. Chem., **36**: 28 (1902).

6. Determination of nitrogen in the form of proteids coagulable by heat in neutral solution.
7. Determination of nitrogen in the form of caseoses (albumoses).
8. Determination of nitrogen in the form of amido-acid compounds.
9. Determination of nitrogen in the form of peptones.
10. Determination of nitrogen in the form of ammonia.
11. Determination of nitrogen in the form of unsaturated paracasein lactate.

1. OBTAINING SAMPLE OF CHEESE.

A sample of cheese is obtained for analysis by means of a cheese-trier, which enables one to secure a round plug of cheese about half an inch in diameter and four to six inches long. Four or five plugs are drawn, one within a short distance of the center of the cheese, one about an inch from the outer circumference, and the others at points equidistant between the two previous ones taken. Samples thus taken represent practically all different conditions existing in the cheese. After each plug of cheese is removed, about an inch of the end having the rind is cut off, and the rest is placed in a well-stoppered, large-mouthed sample bottle. The end with the rind is dipped once or twice in melted paraffin and then carefully replaced in the cheese, being pushed in a little below the surface. After all the plugs have been taken and the ends properly replaced in the cheese, some of the melted paraffin is poured over the surface to fill up and surround the depressions made by replacing the ends of the plugs. This treatment generally insures the exclusion of molds and prevents abnormal loss of moisture in the portions of cheese near the holes left by the removal of the cheese plugs. This is a matter of much importance, when one intends to keep the same cheese for one or two years for systematic examination.

When all the plugs of cheese needed have been taken, the analysis should not be long delayed. The cheese in the bottle is cut into small pieces with a spatula and stirred within the bottle, in order to mix the whole into as homogeneous a mass as possible.

2. DETERMINATION OF TOTAL NITROGEN IN CHEESE.

We weigh out 1 or 2 grams of the cheese, prepared as described above, for the determination of total nitrogen and treat it according to the Kjeldahl-Gunning method, modified as follows: When the solution has become partially digested, we add a piece of copper sulphate about as large as an ordinary pea. Unless this is done, it will take a long time to convert the organic nitrogen completely into ammonia.

3. EXTRACTION OF WATER-SOLUBLE PRODUCTS.

In a porcelain mortar, we thoroughly mix 25 grams of our cheese sample, prepared as indicated above, with about an equal bulk of clean quartz sand. This mixture is transferred to a 450-cc Erlenmeyer flask, to which we add about 100 cc of distilled water at a temperature of 50° C. The flask is then placed on a water bath or in some place where it can be kept at a temperature of 50 to 55° C., and is allowed to stand for half an hour, being vigorously shaken from time to time. The liquid portion is then decanted through a filter of absorbent cotton into a 500-cc flask. The residue is again treated with 100 cc of water, heated, agitated, and the liquid decanted as before. This process is repeated until the filtrate, after being cooled to room temperature, amounts to 500 cc, exclusive of the fat, which usually is present at the top of the liquid.

The cotton filter mentioned is made of two layers of absorbent cotton prepared as follows: In a glass funnel, we place some absorbent cotton to the depth of about 1 inch; moisten this with water, in order to compact it, and then above this place another layer of cotton of the same thickness. Upon this we pour our portions

of cheese extract. This kind of filter allows rapid filtration without the aid of a pump, and is as effective in every way as paper, which requires half a day or more for complete filtration of 500 cc of extract. Several samples of cheese can be extracted at the same time. The upper layer of cotton holds all solid particles and can be returned to the flask for extraction with salt solution.

The method of making a water extract of cheese, as described above, insures the complete removal of all water-soluble nitrogen compounds present in the cheese without danger of coagulating any soluble proteids. The use of water at room temperatures is not, in our experience, equally effective in making a complete extraction of the water-soluble products. Under some conditions, as in the early stages of ripening cheese at low temperatures, small amounts of a body are extracted by water which is precipitated by heat in neutral solution. We are unable to say at present whether this body consists of acid salts of paracasein or of hetero-caseose, which are practically insoluble in water, or whether it is some other compound. The temperature of 50° C. also has the advantage of arresting further peptic or tryptic action during the extraction. The use of acids in extracting cheese is to be avoided, since a small amount of acid will not only precipitate the soluble nuclein, but may form salts with paracasein, which are somewhat soluble in a slightly acid solution; the amount of dissolved paracasein salts under such circumstances depends on the amount of acid used and the time of extraction.

4. DETERMINATION OF TOTAL WATER-SOLUBLE NITROGEN.

For the determination of the amount of total water-soluble nitrogen, we take 50 cc of the water extract, prepared above, equivalent to 2.5 grams of cheese, and treat it according to the Kjeldahl method for determining nitrogen.

5. DETERMINATION OF NITROGEN IN THE FORM OF PARANUCLEIN (PSEUDONUCLEIN).

To 100 cc of the water extract, equivalent to 5 grams of cheese, we add 5 cc of a 1 per cent solution of hydrochloric acid, and warm the mixture on the water bath at 50 to 55° C. until complete separation takes place, as shown by a clear supernatant liquid. The precipitate is filtered, washed with water, and then, with the filter paper, treated by the Kjeldahl method to determine the amount of nitrogen. The nitrogen equals nitrogen present in the form of paranuclein (pseudonuclein.)

In our early work 2 or 3 cc of a saturated alum solution were used for this determination, for the reason that in the separation of casein in milk we had used this reagent successfully; but at the time the nature of the body we were precipitating from our water solution of cheese was not known. Later, when we had studied it and learned its character it was found, on comparing precipitations, by use of alum and by hydrochloric acid that alum gave high results, undoubtedly precipitating some caseoses. In 27 comparative trials with water extracts of different cheeses, we found in the alum precipitate nitrogen varying from 0.2 to 0.337 per cent of the cheese and averaging 0.269 per cent, while the nitrogen in the hydrochloric acid precipitate varied from 0.046 to 0.145 per cent of the cheese and averaged 0.085 per cent. The nitrogen precipitated by alum in these 27 cases was from 2.1 to 5.5 times as much as that precipitated by hydrochloric acid, the average of all being 3.2. Since hydrochloric acid is known to precipitate paranuclein completely, we are justified in assuming that the alum precipitates other compounds, and this is confirmed by other work, showing that when alum is used as the first precipitant we get smaller quantities of caseoses in the filtrate than we do when we use hydrochloric acid as the precipitant of paranuclein. Alum appears to resemble zinc sulphate as a precipitant of proteids.

Paranuclein (pseudonuclein) results from the breaking down of casein or paracasein and is always found in the water extracts of ripening cheese, whether salted or unsalted. It may, perhaps, be regarded more accurately as a residue and proba-

bly should not be counted as one of the products to be used in measuring the extent of cheese ripening. This is undoubtedly the same body as Chittenden's dyspeptone,[a] which he found as an insoluble residue in a pepsin-hydrochloric-acid digestion of casein.

6. DETERMINATION OF NITROGEN IN THE FORM OF PROTEIDS COAGULABLE BY HEAT IN NEUTRAL SOLUTION.

The filtrate from the preceding determination (5) is made neutral with dilute caustic potash, using phenolphthalein as an indicator. It is then heated at the temperature of boiling water, until any coagulum that forms settles completely, leaving a clear supernatant liquid. The precipitate is washed with water and its nitrogen determined by the Kjeldahl method. In our experience, such a precipitate rarely occurs, except in the case of cheese ripened near freezing point. The nature of this body we have not yet investigated.

7. DETERMINATION OF NITROGEN IN THE FORM OF CASEOSES (ALBUMOSES).

The filtrate from the preceding determination (6) is treated with 1 cc of 50 per cent sulphuric acid, saturated with chemically pure zinc sulphate and then warmed to about 70° C. until the caseoses separate completely and settle. The mixture is allowed to cool and is then filtered. If filtered hot, there will occur a further separation of caseoses in the filtrate on cooling. The precipitate is washed with a saturated solution of zinc sulphate made slightly acid with sulphuric acid. The nitrogen in the precipitate is determined by the Kjeldahl method.

For the determination of caseoses, the use of ammonium sulphate was exclusively employed until Bömer[b] proposed the use of zinc sulphate, which possesses a distinct advantage in enabling one to determine nitrogen directly in the precipitate or filtrate. This method has been employed, in the estimation of caseoses, also by the Wisconsin Agricultural Experiment Station. In the present state of our knowledge of this class of compounds, zinc sulphate must be regarded as the most available reagent for their quantitative separation.

8. DETERMINATION OF NITROGEN IN THE FORM OF AMIDO-ACID COMPOUNDS.

The amido-acid compounds are determined in the filtrate from the precipitation of peptones (9). For the removal of peptones three reagents have been commonly used: (1) Tannin and sodium chlorid, (2) phosphotungstic acid with sulphuric acid, and (3) bromin with hydrochloric acid. After the removal of peptones the filtrate contains amido-acid and ammonia compounds. After determining the amount of total nitrogen in this filtrate and then the amount of nitrogen present in the form of ammonia (as obtained in 10, p. 97), we subtract the amount of ammonia nitrogen from the combined amount of amido-acid and ammonia nitrogen and thus obtain the amount of amido-acid nitrogen. In the following section (9) we describe the methods involved in removing peptones by the different reagents and the efficiency of each reagent.

9. DETERMINATION OF NITROGEN IN THE FORM OF PEPTONES.

(*1*) *By tannin and sodium chlorid.*

We place 100 cc of our water extract of cheese in a 250-cc graduated flask, add 1 gram of sodium chlorid and a solution containing 12 per cent of tannin until one drop added to the clear supernatant liquid gives no further precipitate. We then dilute to the 250-cc mark, shake, filter through a dry filter, and determine the

[a] Studies in Physiol. Chem., Yale Univ., **3**:66 (1887–88).
[b] Zeit. Analyt. Chem., **5**:562 (1895).

amount of nitrogen in 50 cc of the filtrate by the Kjeldahl method; this gives us the amount of nitrogen in the form of amido-acid and ammonia compounds. The amount of nitrogen in the form of peptones is determined by difference—that is, by subtracting from the amount of total nitrogen in the water extract the combined sum of the amounts of nitrogen found in 5, 6, 7, 8, and 10.

The combination of tannin and salt has been settled upon by us as the most satisfactory for the separation of casein-derived peptones from amido-acid compounds in milk and cheese analysis, when, as is commonly the case, we have large amounts of amido-acid compounds relative to peptones. We have confirmed Schjerning's [a] results showing that this reagent does not precipitate the monoamido-acid compounds, such as leucin, tyrosin, aspartic acid, glutamic acid, and amidovaleric acid, nor does it precipitate histidin, arginin, lysin, cadaverin, putrescin, lysatin, or ammonia. In our work the tannin-salt solution has nearly as great a precipitating power as phosphotungstic acid, precipitating 93.3 per cent of the total nitrogen compounds present in a sample of fresh milk; in a study of ripened cheese it precipitated the uncrystallizable end products, caseoses and peptones, so completely that no further trouble was experienced in separating the crystallizable end products.

It is well to record here the fact that when precipitation of peptones with tannin-salt solution is attempted in a mineral acid solution no precipitate occurs; it is only in neutral solution that more complete precipitation takes place.

The chief objection to the use of tannin-salt solution as a means of separating caseoses and peptones from amido-acid compounds and ammonia is that it is not a complete precipitant of peptones. Hence, when the reagent for this separation is used we commonly leave some peptones to be estimated as amido-acid compounds, the amount of peptones thus being made smaller and the amount of amido-acid compounds larger than the quantity actually present. Under the discussion of the use of phosphotungstic acid as a reagent for separating these classes of nitrogen compounds are given for comparison some results secured by each of the two reagents.

(*2*) *By phosphotungstic acid with sulphuric acid.*

In a 250-cc graduated flask we place 100 cc of the water extract of cheese, add 100 cc of water and then 5 cc of strong sulphuric acid. To this add phosphotungstic acid of 30 per cent strength until one drop gives no further precipitation in the clear supernatant liquid. Then dilute to the 250-cc mark and filter through a dry filter. In 50 cc or 100 cc of this filtrate we determine the amount of nitrogen by the Kjeldahl method, and then the amount of peptones is obtained by difference.

Phosphotungstic acid has come into very general use in this country and in Europe as a means of separating peptones from amido-acid compounds in work with cheese and milk. The results of Stutzer [b] and of Bondzynski [c] agree in showing that phosphotungstic acid is a complete precipitant of casein, caseoses, and peptones, while in their experience it does not precipitate the amido-acid compounds or ammonia. Freudenreich and Jensen, in all their work, even of recent date, have used this reagent in the cold as a means of separating peptones from amido-acid compounds. Babcock, Russell, and Vivian, in this country, have used it, as well as tannin, designating the different precipitates as "peptones by phosphotungstic acid" and "peptones by tannin."

In the introductory portion of this paper, when mentioning different cleavage products of casein, we included among them the hexon bases, viz, arginin, histidin, and lysin; and, in addition, certain compounds resulting from their cleavage, such as putrescin and cadaverin, and also pyrrolidin-α-carbonic acid, all of which are precipitated by phosphotungstic acid. While all these products have not been sepa-

[a] Zeit. Analyt. Chem., **39**: 545 (1900).
[b] Zeit. f. analyt. Chem., **35**: 1493 (1896).
[c] Landw. Jahrbuch der Schweiz (1894).

rated from ripening cheese, it is probable that they will be sooner or later. We shall soon publish results of work done in this laboratory showing in normal ripening cheese the presence of histidin, lysin, putrescin (derived from arginin[a]), and Siegfried's lysatin, which is also precipitable by phosphotungstic acid. The quantities of these bases that can be derived from casein are not to be neglected, since, for example, in a hydrochloric-acid cleavage 15.4 per cent of the nitrogen of the products splits off into the hexon bases. Bondzynski has used phosphotungstic acid in hot solution with arginin, and finds the precipitate soluble when hot, separating out on cooling; and this statement we can confirm, the solution, however, being complete only on boiling. In the case of lysin, histidin, and putrescin the phosphotungstic-acid precipitate fails to redissolve completely at the temperature of the water bath or on boiling. This behavior renders worthless the use of phosphotungstic acid as a reagent for the separation of peptones from those amido-acid compounds that are precipitated by it.

We have seen that tannin-salt solution fails to precipitate peptones completely, and that phosphotungstic acid precipitates, in addition to peptones, some amido-acid compounds. When, therefore, we use these two reagents in precipitating solutions that contain both peptones and amido-acid compounds, as in the case of normal-ripening cheese, we should expect to find the amount of nitrogen compounds left in the filtrate less with phosphotungstic acid than with tannin. This is found invariably to be the case. Vivian [b] has published some results obtained with nine different cheeses, which illustrate this point. We give his figures in the table following:

TABLE I.—*Comparison of phosphotungstic acid and tannin-salt solution in precipitating the nitrogen compounds contained in water extracts of cheese.*

Precipitating agent used.	Numbered samples.									Average.
	1.	2.	3.	4.	5.	6.	7.	8.	9.	
	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.
Phosphotungstic acid	1.08	1.00	0.82	0.63	0.67	1.69	0.95	1.10	1.22	1.02
Tannin-salt solution	1.54	1.26	1.12	.65	1.16	1.87	1.08	1.36	1.42	1.27

In connection with the above results nothing was stated in regard to the history of the cheeses used in the work. We have studied the action of phosphotungstic acid and tannin-salt solution in connection with samples of cheese that were under known well-controlled conditions, thus learning something of the general character of the proteolytic changes taking place. Twenty-five grams of cheese curd were placed in each of several Erlenmeyer flasks, 50 cc of water added, and the contents sterilized by heat. We then added 0.5 gram of concentrated lactic acid, in order to convert the paracasein into unsaturated paracasein lactate. [c] To some of the flasks thus prepared sterilized pepsin was added, and to others sterilized rennet extract. For this purpose the enzyms were prepared as follows: We dissolved 600 milligrams of Parke Davis & Co.'s aseptic pepsin in 25 cc of water, added 0.5 per cent of formalin (containing 40 per cent of formaldehyde), and let the solution stand until bacteriological examinations, made by Mr. H. A. Harding, showed the absence of living organisms. The mixture was then diluted to 100 cc with water, and to each flask containing cheese we added 10 cc of this sterilized-pepsin solution. One thousand parts of the mixture in each flask thus contained one part of pepsin.

In preparing the sterilized rennet solution, 5 cc of Hansen's rennet extract were diluted to 25 cc with water, 0.5 per cent of formalin was added, the completeness of

[a] A. Ellinger, Ber. deut. chem. Ges., **31**: III–3183 (1898).
[b] Ann. Rept. Wis. Exp. Sta. **16**: 171 (1899).
[c] N. Y. Agr. Expt. Sta. **214**: 67 (1902).

sterilization proved by bacteriological examinations, diluted to 100 cc and 10 cc of this preparation added to each flask containing cheese.

The flasks thus prepared were kept at 15.5° C. The analytical results given below were obtained at the end of two and four weeks. In this work, we had only the enzyms of pepsin and of rennet pepsin acting upon our proteid. Under these conditions, especially in the given length of time, we should not expect the formation of any considerable amount of amido-acid compounds precipitable by phosphotungstic acid. The results obtained are given in the following table:

TABLE II.—*Comparison of phosphotungstic acid and tannin-salt solution in precipitating the nitrogen compounds formed by peptic digestion of cheese.*

Precipitating agent used.	Numbered samples.								
	1.	2.	3.	4.	5.	6.	7.	8.	Average.
	P. ct.	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*
Phosphotungstic acid	0.10	0.10	0.150	0.175	0.10	0.08	0.16	0.16	0.123
Tannin-salt solution	.45	.44	.645	.685	.48	.46	.73	.70	.574

In every case except one, the amount of nitrogen not precipitated by tannin-salt solution was more than four times the amount obtained by phosphotungstic acid. No ammonia was present in any case. In view of these widely differing results in relation to the amounts of amido-acid compounds found, the questions may be asked: "Which reagent more nearly represents the amount of amido compounds actually present? Does the tannin-salt reagent fail to precipitate the peptones completely, thus allowing the unprecipitated peptones to be counted among the amido-acid compounds? Or does the amount of nitrogen in the filtrate in case of this reagent really represent amido-acid compounds? Does the phosphotungstic acid precipitate some of the amido compounds simultaneously with the peptones, thus cutting out a part of the amido-acid compounds and counting that part among the peptones? Or is there in the cheese only the small amount of end products indicated by the action of the phosphotungstic acid?"

While we did not by individual isolation determine to what extent amido compounds were present, we are justified in believing that such compounds were not yet present in the cheese in any appreciable degree; and, hence, the figures obtained with phosphotungstic acid are much nearer the truth than those obtained by tannin-salt precipitation. The reasons for this belief are as follows: The amido compounds precipitated by phosphotungstic acid are known to be chiefly the diamido compounds, while the monoamido compounds are precipitated little, if at all. Hence, the compounds found in the filtrate of a phosphotungstic acid precipitation are mainly monoamido compounds. Now let us assume temporarily that the amounts of nitrogen in the tannin-salt filtrate, given in the table above, represent the total amido compounds, free from peptones; then, since the monoamido compounds are represented by the amounts of nitrogen obtained in the phosphotungstic acid filtrate, the difference between the two sets of figures—that is, those obtained by tannin salt solution and those obtained by phosphotungstic acid—represents the amount of diamido compounds. Taking the average of the results given in the table above, the nitrogen of the total amido compounds is 0.574 per cent of the cheese, while the nitrogen of the monoamido compounds is 0.128 per cent of the cheese, thus leaving the difference as the nitrogen of the diamido compounds, equivalent to 0.446 per cent of the cheese. According to these figures, the monoamido compounds constitute about 22 per cent of the entire amount of amido bodies, while the remainder, 78 per cent, represents largely diamido compounds. In this case, the ratio of monoamido to diamido compounds is as 1 to 3.5. Keeping these data in mind, we will call attention

to some work done by Hart [a] in studying the cleavage end products formed by the action of hydrochloric acid on casein. He found that the diamido compounds formed less than 20 per cent of the total amido compounds, so that the ratio of monoamido to diamido compounds was as 1 to 0.25 or less; in other words, the monoamido compounds were greatly in excess of the diamido compounds or just the reverse of what we find to be the case in the results embodied in the table above, based on the assumption that the nitrogen in the tannin-salt filtrate represents the total amido compounds and nothing more. The most obvious and rational explanation of this discrepancy observed in the ratio of monoamido to diamido compounds is that it is wrong to assume that the tannin-salt filtrate contains only amido compounds and not any peptones. Withdrawing that assumption, then, and allowing that the nitrogen in the tannin-salt filtrate represents some peptones as well as the amido compounds, how can we tell in this particular case the true amount of amido compounds in the cheese? Unquestionably the results with phosphotungstic acid more nearly represent the truth in regard to the amido compounds, because under the conditions of the experiment we should expect very small amounts of amido compounds, if any; and in this particular case the amounts are so small as practically to indicate the absence of amido bodies altogether. From this it may be seen that it is possible for the tannin-salt reagent to give results that are decidedly misleading.

(3) *By bromin with hydrochloric acid.*

To the filtrate from the zinc sulphate precipitate (7) we add 2 or 3 drops of strong hydrochloric acid and then bromin until the liquid becomes saturated and there remains after vigorous agitation an undissolved globule of bromin, amounting to 0.5 cc to 1 cc. This is allowed to stand over night. The precipitate is then filtered and washed with bromin-saturated water. The nitrogen in the precipitate is then determined by the Kjeldahl method and is called nitrogen in the form of peptones, the filtrate containing the amido-acid compounds and ammonia.

The use of chlorin by Rideal and Stewart [b] in precipitating proteids suggested to Allen and Searle [c] the use of bromin. They reported that bromin quantitatively precipitates the products formed by the peptic digestion of egg albumin and they developed the method practically as given above. As applied to the separation of peptones from amido-acid compounds in cheese and milk, the method gives varying results, depending upon the age of the cheese or milk used.

In the case of our water extracts made from cheese nine months to a year old, crystalline bodies in noticeable quantities are precipitated by bromin along with peptones, owing probably to the presence of tyrosin, giving the solution a turbid appearance and rendering filtration difficult. Schjerning [d] has shown that tyrosin behaves in this manner with bromin water. This precipitate is partly retained on the filter paper and is estimated as peptone.

Schjerning has shown also that bromin does not completely precipitate milk proteids and their derived caseoses and peptones. Of the whole proteid he obtained only 76.7 per cent by bromin. In the case of milk we have obtained results varying with the age of the milk. In perfectly fresh milk, when the amount of amido compounds must have been least, we obtained 91.3 per cent of the entire milk proteids by bromin precipitation. In another case of fresh milk we compared the precipitation of proteids by bromin and hydrochloric acid with that by tannin and sodium chlorid and by solution of phosphotungstic acid and sulphuric acid, with the following results: There was precipitated—

By phosphotungstic and sulphuric acids, 93.8 per cent of the total nitrogen.

By tannin and sodium chlorid, 93.3 per cent of the total nitrogen.

By bromin and hydrochloric acid, 91.5 per cent of the total nitrogen.

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[a] Zeit. f. Physiol. Chem., **33**:347 (1901).

[b] Analyst, **22**:228 (1897).

[c] Analyst, **22**:259 (1897).

[d] Zeit. f. Anal. Chem., **39**:545 (1900).

There is also a possible source of error in connection with the use of bromin in precipitating peptones when the filtrate from the bromin precipitate is used directly for the determination of amido-acid compounds. We have found in the case of water extracts from cheese over one year old that there is an actual loss of nitrogen when bromin is allowed to stand in contact with the water extract. In the case of one cheese two years old, the cheese extract, consisting of caseoses, peptones, and amido-acid compounds, contained nitrogen equivalent to 2.74 per cent of the cheese before adding bromin, while, after standing one hour in contact with bromin in hydrochloric-acid solution, there remained only 1.52 per cent of nitrogen; in other words, there had disappeared 44.6 per cent of the nitrogen present before the addition of bromin. In cheese one year old we have found the loss varying from nothing in one case to over 5 per cent in others. To show whether or not this loss came from the action of bromin on the caseoses or peptones we removed the caseoses with zinc sulphate, and in another sample of cheese extract we removed the caseoses and peptones with phosphotungstic acid, and the loss still occurred. By passing a current of air through the above extract in contact with bromin and then through potassium hydroxid and through sulphuric acid, these reagents were found free from nitrogen compounds, indicating that the lost nitrogen disappeared in the form of free nitrogen and not in the form of ammonia or nitrogen oxids. We can not regard the method of determining the amount of peptones in cheese extracts by means of bromin as a reliable method, because (1) bromin precipitates small amounts of tyrosin and perhaps certain other similar compounds; (2) it is not a complete precipitant of caseoses and peptones; and (3) its filtrate can not be used for the determination of amido-acid compounds, especially in old cheeses, owing to the decomposing effect of bromin upon such compounds, setting nitrogen free. In addition, bromin is a most disagreeable reagent to handle.

(*4.*) *Comparative value of different reagents used in separating peptones and amido-acid compounds.*

We have now considered in some detail each of the three reagents most commonly used in separating peptones from amido-acid compounds, viz: (1) Tannin-salt solution, (2) phosphotungstic acid with sulphuric acid, and (3) bromin with hydrochloric acid. Tannin-salt solution fails as a perfect reagent for the separation, because it does not completely precipitate peptones, which results in making the quantitative results for amido-acid compounds too high and may indicate the presence of considerable quantities of amido compounds even when they are practically absent. Phosphotungstic acid, on the other hand, completely precipitates peptones, but also precipitates some of the amido-acid compounds that are present in cheese and milk, and the consequence is that the amount of amido-acid compounds found is too low. Bromin is open to both objections—it fails to precipitate peptones completely and at the same time does precipitate some of the amido-acid compounds. While these two sources of error might tend to offset each other under certain conditions, we can not depend upon such a method for reliable quantitative results.

In our judgment, it is desirable, for best results, to use phosphotungstic acid to separate peptones and amido-acid compounds when the amount of amido-acid compounds is relatively small as compared with peptones or when they consist mostly of monoamido compounds. This condition occurs in the early stages of cheese ripening and persists longer in cheese cured at low temperatures; it occurs also in milk and cheese acted upon by pepsin enzyms, especially in the presence of chloroform.

Tannin-salt solution can be relied upon to give better results than phosphotungstic acid when amido-acid compounds are present in proportions that are relatively large compared with peptones or when they consist largely of diamido compounds. The former condition prevails in normal cheese cured under usual conditions, especially after the first few weeks of curing.

10. DETERMINATION OF NITROGEN IN THE FORM OF AMMONIA.

Distill with magnesium oxid 100 cc of the filtrate from the tannin-salt precipitation, passing the distillate into a standardized acid and titrating in the usual way. In our early work the cheese mass itself, suspended in water, was used for distillation, giving slightly higher results than the method just described. The small increase is generally accounted for as coming from the proteids themselves present in the solution. Theoretically it is true that when such bases are present as putrescin and cadaverin they might distill with the ammonia. In one case, where a large quantity of cheese was subjected directly to distillation with magnesium oxid and the distillate examined for these bases, none was found, the distillate consisting entirely of the ammonia salt. The high boiling points of cadaverin and putrescin and the consequent difficulty of distilling them with steam probably accounts for their absence in the distillate.

In our early work on the determination of ammonia in milk and cheese we subjected to distillation with magnesium oxid and with barium carbonate many different amido compounds in order to ascertain if any of these bodies when pure could split off basic nitrogen. While some of the products used in our work are not at all likely to be found in cheese or milk, we include them with the others in the list given below. The method was carried out as follows: Dissolve 1 gram of each amido body, or if insoluble, suspend it in 50 cc of water, and for distillation use 10 cc of this mixture diluted to 150 cc, adding magnesium oxid or barium carbonate and using ordinary atmospheric pressure.

Amido bodies used were—

Acetamid.	Diphenylamin.	Phenylenediamin.
Allantoin.[a]	Glutamic acid.	Trimethylamin.
Arginin.	Glycocoll.	Tyrosin.
Aspartic acid.	Histidin.	Uric acid.
Creatin.	Leucin.	Xanthin.
Creatinin.	Lysin.	

The result of this work was that nothing was distilled over with either magnesium oxid or barium carbonate in any case except that of trimethylamin, the nitrogen of which was all obtained in the distillate with both regents.

We have also used the excellent Nencki apparatus, distilling under reduced pressure the filtrate from the tannin-salt precipitation. In comparative trials we have obtained no lower results than when we distill under ordinary atmospheric pressure.

11. DETERMINATION OF NITROGEN IN THE FORM OF UNSATURATED PARACASEIN LACTATE.

The residue insoluble in water is treated with several portions of a 5 per cent solution of sodium chlorid, the process being carried out as in preparing the water extract (3, p. 89). The nitrogen in an aliquot part of the 500 cc of this salt extract is determined by the Kjeldahl method.

II. Methods for the Separation and Estimation of the Nitrogen Compounds of Milk and their Proteolytic Products.

We will briefly describe the methods used for the separation and estimation of the nitrogen compounds of milk and their proteolytic products in the following order:

1. Determination of total nitrogen in milk.
2. Determination of nitrogen in the form of casein.
3. Determination of nitrogen in the form of albumin and syntonin.
4. Determination of nitrogen in the form of caseoses.
5. Determination of nitrogen in the form of amido-acid compounds.
6. Determination of nitrogen in the form of peptones.
7. Determination of nitrogen in the form of ammonia.

[a] Zeit. f. Physiol. Chem. 34: 145 (1901).

1. DETERMINATION OF TOTAL NITROGEN IN MILK.

Weigh about 5 grams of milk and determine the nitrogen by the Kjeldahl method.

2. DETERMINATION OF CASEIN.

To about 10 grams of milk add 90 cc of water at 104 to 108° F. (40 to 42° C.) and then 1.5 cc of 10 per cent acetic acid. Agitate and warm at the temperature given above until a flocculent precipitate separates, leaving a clear supernatant liquid. Filter, wash, and treat by the Kjeldahl method for estimating nitrogen.

In fresh milk, 2 or 3 cc of a saturated solution of alum may be used in place of acetic acid, usually with little higher results. But when the milk casein has been proteolyzed to any extent, the use of alum is not permissible, since it precipitates caseoses in addition to casein.

The use of acetic or any other acid in precipitating casein in milk, whose casein has been digested in any degree, precipitates, in addition to casein, any paranuclein that is present. We have not yet succeeded in devising satisfactory methods for the separation of these two compounds.

3. DETERMINATION OF NITROGEN IN THE FORM OF ALBUMIN AND SYNTONIN.

The filtrate from 2 is neutralized by caustic alkali, using phenolphthalein as indicator, and is then heated at the temperature of boiling water until the precipitate completely separates and settles. The precipitate is then filtered, washed, and treated by the Kjeldahl method.

4. DETERMINATION OF NITROGEN IN THE FORM OF CASEOSES.

The filtrate from 3 is heated to 70° C., 1 cc of 50 per cent sulphuric acid is added and then chemically pure zinc sulphate to saturation. Let stand at the temperature indicated until the caseoses completely separate and settle. Then cool the mixture, filter, wash with a saturated solution of zinc sulphate made slightly acid with sulphuric acid, and treat the precipitate by the Kjeldahl method.

5. DETERMINATION OF NITROGEN IN THE FORM OF AMIDO-ACID COMPOUNDS.

Treat about 50 grams of milk with a tannin-salt solution or with phosphotungstic acid according to directions given under 8, p. 91.

6. DETERMINATION OF NITROGEN IN THE FORM OF PEPTONES.

From the total nitrogen, subtract that found in all forms other than that of peptones, as indicated under 9, p. 91.

7. DETERMINATION OF NITROGEN IN THE FORM OF AMMONIA.

See under 10, p. 97.

III. DETERMINATION OF CHLOROFORM.

When chloroform is used as an antiseptic in milk and cheese it is very essential to know approximately the amount present, in order that we may have a proper control of conditions. We have used the following method successfully: Place 5 grams of milk or cheese in a pressure bottle with about 100 cc of alcohol and 5 grams of caustic potash. The bottle is then heated in an autoclave for half an hour at 110° C. The resulting chlorid is determined by titration, as for chlorin in sodium chlorid.

RECOMMENDATION.

It is recommended that the methods presented above be adopted as provisional methods under the head of dairy products.

Mr. Bigelow. I would like to ask if the referee has tried precipitating with bromin in the presence of zinc sulphate. Some time ago we examined meat extracts by dividing the filtrate from the proteoses (coagulated by neutralization and boiling) into several portions, and precipitated one portion with bromin and another with zinc sulphate. It was expected that bromin would precipitate both proteoses and peptones, whereas zinc sulphate would not precipitate peptones. Mr. Trescot, who was doing this work, was very much surprised to find that the zinc sulphate precipitate was greater than the bromin precipitate.

The President. If there is no objection on the part of the association I would like to introduce the president of the Columbian University.

ADDRESS BY PRESIDENT NEEDHAM COLUMBIAN UNIVERSITY.

Mr. President and Gentlemen of the Association: It would be the height of presumption for me to undertake to discuss any of the matters which this distinguished body of chemists is considering. I belong to another profession, and in these days one profession is quite enough for one man. I come to extend my congratulations upon this large and representative gathering of your association; to welcome you on behalf of Columbian University to this building, and to offer you all the accommodations and facilities at our disposal for your meetings. We are honored and delighted to have scientific men come here and discuss in public meetings the progress and results of their work; it is one of the great features of Washington life and is due in a great measure to the fact that we have so many eminent scientific men here engaged in professional work. The number employed by the Government is little known. I was much interested in a statement made to me by an official at the time Mr. Carnegie made his noble gift to found in this city an institution for original research. I said to this gentleman, "What a great sum of money Mr. Carnegie has given to scientific work." And he replied, "Yes, ten millions is a large sum, but do you know what the Government of the United States is doing for science?" I replied that I did not. And then he told me that the amount of money expended annually by the Government for scientific work represented an annual interest of 2½ per cent upon $200,000,000.

I have been desirous to secure the services of some eminent men, who are in larger and older institutions, for this university, and feared that they could not be induced to come for the reason that they would have to leave the association and intellectual atmosphere of the older universities, but I was pleased to be told by a most distinguished educator that this would not prevent their coming—"Because," he said, "you have so many distinguished scientific men in the Departments of the Government among whom they would find association in the city if it were not found to a sufficient degree in the university."

A few years ago I was crossing the Atlantic, homeward bound, and saw among the passengers three very distinguished looking men. They were always together, and much absorbed in earnest conversation. I overheard them speaking of their "profession" with great respect and veneration. I thought they must be clergymen. I learned that two of them were from a German and one from an English university, and their "profession" was chemistry. It was then something new for me to hear chemistry spoken of in such exalted terms as a profession. It impressed me, and set me to thinking. I recalled that the greatest service, and, therefore, the greatest nobility, lies along the path of discovering the elements and forces of nature; the way in which these forces may be made serviceable to man; in short, discovering the laws of nature. It has been said that the great object of education should

be to acquire the knowledge of some one thing, and hold it with such a grip as to make it of practical value to mankind. We are passing away from the old thought that only the mysterious is divine, to the broader and better thought that an understanding of the laws of nature is also a revelation of the divine thought. There can be no higher or nobler calling than that in which men, enthusiastic with a desire to know the truth, are seeking and unfolding a knowledge of the uses and laws of matter. When we look about and undertake to enumerate the things which science is doing for the good of man, we must be profoundly impressed with the fact that if these results could be withdrawn the world would be deprived of its richest treasures. No greater service has been rendered to this great land in the development of its almost boundless natural resources than by the scientists of America. They have purified the foods that nourish us; they have multiplied and cheapened the products of the mines and the factories; made the fields yield larger and richer harvests; and made the desert "to blossom as the rose."

I welcome you here, and congratulate you upon the dignity of your labors, the nobility of your calling, and the splendid achievements of your profession.

The PRESIDENT. I am sure that I express the feeling of every member of the association in thanking Mr. Needham most cordially for his appreciative and inspiriting words.

If there are no other papers to be read on the separation of nitrogenous compounds we will proceed to the discussion of the subject.

Mr. VAN SLYKE. In discussing the matter from the standpoint of the paper read this morning it should be remembered that, while some general methods may be applied to the nitrogen compounds obtained from different sources, as from meat and vegetables, we can not expect that one man can go to work and apply the same method in a wholesale way to each of these different groups of compounds, until we know something more in detail concerning the individual compounds and their chemistry. So, while from personal reasons, and on account of the character of the investigation we are carrying on we have given attention exclusively to this side of it, we do not mean to imply that these methods have a general application. The same kind of work must be done for each class of compounds, and we are liable to fall short in our appreciation of the enormous amount of work involved and of the great number of compounds with which we have to deal. I do not offer this as an apology for the work which we have done, but simply as an explanation of the paper presented and the large amount of work which remains to be accomplished.

The PRESIDENT. I am sure every member of the association appreciates the character of the work which Mr. Van Slyke and Mr. Hart have done, and we know that one man can not be expected to cover the field. It might be possible to associate the best experts in the country with the work in connection with meat extracts and cheese and vegetable products. This would seem to be a matter worthy of consideration.

If there is no further discussion on this question, we will hear the report on soils.

REPORT ON SOILS.

By F. P. Veitch, *Referee.*

Your referee did not know until the receipt of Dr. Wiley's notification in March that he had to serve in this capacity. Upon receipt of this notice, samples were solicited and the following circular letter requesting cooperation and outlining the work was sent to the chemists of all the stations and of the U. S. Department of Agriculture. Only eight promised to cooperate in any part of the work.

Outline of Proposed Work on Soil Samples for 1902.

Dear Sir: Below you will find an outline of the proposed work on soils for this year. The work is divided into three parts, one or more of which you are asked to take up, notifying the referee of your selection.

(1) The determination of available phosphoric acid.
(2) The determination of available potash.
(3) The analyses of alkali soils and crusts.

The samples for the first two lines of work have been selected very carefully from the permanent fertilizer plats of several of the experiment stations and represent soils differing greatly in physical as well as chemical conditions.

The methods with which it seems most desirable to work are indicated under each heading. At the same time the referee would be pleased to have comparative results by other methods, for which, of course, full credit will be given.

As it is not probable that one worker will be able to assist in all the work outlined, each is asked to select the line or lines which he feels he can undertake, and notify the referee, who will forward appropriate samples.

It is hoped that three or four careful workers will make determinations of available plant food by the N/200 HCl method and that others will make determinations by the N/5 HCl method.

The referee would urge upon the members of the association the desirablity of a more hearty cooperation in the study of methods for soil investigations, and to this end he would suggest to those holding professorships in their respective State colleges the suitability of this line of investigation for a portion of the work required for the Master's degree.

Determination of moisture is to be made by the official method, Bureau of Chemistry, Bulletin No. 46, revised, page 71. Calculate all results to a free-water basis.

1. *Determination of available phosphoric acid.*

(It is asked that in work on this subject preference be given the N/200 HCl method.)

(*a*) By the N/200 HCl method (Jour. Am. Chem. Soc., 24, p. 79).
(1) Follow the method strictly as given, except do not correct for basicity of sample.
(2) Uniform temperature (40° C.) and agitation must be secured. Use Wagner machine.
(3) Results should be corrected by blanks used on reagents.
(*b*) By the N/5 HCl method (Bulletin No. 46, revised, p. 74).
(1) Uniform temperature (40° C.) and agitation must be secured. Use Wagner machine.

2. *Determination of available potash.*

(*b*) By the N/200 HCl method.
(1) Prepare solution as for the determination of phosphoric acid.
(2) Results should be corrected by blanks on reagents.
(*c*) By the N/5 HCl method.
(1) Use a portion of the solution secured for phosphoric acid determination.
(2) Correct results by using blank on reagents.

3. *Analysis of alkali soils and crusts.*

By direction of the association the methods of alkali analyses as carried out in the Bureau of Soils, United States Department of Agriculture, were referred to the referee for study and report.

For this work no samples will be furnished by the referee, but those interested in this line of work are requested to give these methods a trial and to suggest such modifications as experience shows will improve them. For these methods see Bulletin No. 18, Division of Soils, page 65.

As the result of some preliminary study the referee would suggest, for the consideration of those interested, the following modifications of the methods:

(*a*) Under "Preparation of solution," page 67, in place of treating 50 grams of soil with a liter of water in the large beaker, the referee suggests that 10 grams be placed in a liter flask, or 5 grams in a half-liter flask, made up to volume, shaken frequently, and allowed to stand overnight.

(*b*) For standard solution of acid potassium sulphate use N/10 sulphuric acid. (North and Lee find that strictly theoretical results are obtained when the point of the burette is below the surface of the liquid being titrated; also that the presence of about one-half gram sodium chlorid in the volume titrated introduces no appreciable error.—Jour. Soc. Chem. Ind., No. 5, XXI, p. 322, 1901.)

(*c*) As indicators in dark solutions, compare methyl orange and Congo red.

(*d*) On page 70, line 26, for "several drops of a solution of phenolphthalein" read "1 cc of a 1 per cent solution of phenolphthalein."

(*e*) On page 72, line 26, for "one drop" read "three drops."

(*f*) As the estimation of the bases begins with lime, a word of caution should be given. Before adding ammonium oxalate, add ammonia in slight excess; and if a precipitate forms, boil, filter, and proceed as usual. This is necessary in soils or crusts containing large amounts of carbonates, which, of course, dissolve some alumina.

All results must be in the hands of the referee by October 1, 1902.

Please notify the referee promptly whether or not you can cooperate in this work.

Yours, very truly,

F. P. Veitch, *Referee on Soils.*

U. S. Department of Agriculture, Bureau of Soils,
Washington, D. C., May 1, 1902.

The Samples.

In soliciting samples for the work the referee has aimed to get soils whose crop and fertilizer history is known accurately for a number of years, and which will be representative of different kinds of soils. In view of the fact that so few cooperate in this work, it has also appeared desirable so to select such samples that soil from these same plats may be used in the future for the association work, if it appears desirable. The referee believes that more will be accomplished by testing various methods on a series of known soils than by trying them on new samples each year, as it will then be possible to compare the results of many workers by several methods on known soils.

The history of the plats before the experiments were started is given in the text under the respective sample numbers. The crop history since the beginning of the experiment now being conducted on these plats is summarized in Table III. In all cases where it is possible the referee has calculated the effect of an essential plant food by subtracting the yield of the plats to which all but this particular plant food was applied from the yields of the plats receiving complete fertilizers.

The referee desires to acknowledge the assistance of the directors and chemists of the several stations, who not only furnished the samples, but in the majority of instances distributed the subsamples to the cooperators.

Directions for taking soil samples.

All samples should be taken from a sufficient number of places in a plat to be thoroughly representative of the plat. The number of places should never be less than two and may be more, being governed by the size and uniformity of the plat.

In taking samples the undecomposed matter on the surface is to be avoided as far as possible.

Samples should be taken to the full depth of the soil; that is, to the change in color, texture, or other conditions usually recognized as marking the line between soil and subsoil, provided this line does not occur at a greater depth than 1 foot. In no case is a sample to be taken to a greater depth than 1 foot.

The depth to which samples are taken should be noted and a statement of the depth should accompany the sample.

Samples should not be taken when the soil is too wet to work.

Sufficient soil should be taken to give about 100 pounds of dry soil which will pass through a 3-mm mesh sieve.

Samples should be dried as quickly as possible at a temperature not over 40° C.

In those cases where the subsamples are distributed directly by the collector, the samples when dry should be passed through a 3-mm sieve, breaking down all lumps with a wooden mallet or rolling pin, the fine and coarse material weighed, and the fine material wrapped in strong paper in packages of about 1 pound.

Cotton sacks and franks will be furnished by the referee for the distribution of the samples.

In addition the referee should be furnished with as full a description as possible of the obvious characteristics of the subsoil, drainage conditions, distance from surface of solid rock when this distance is less than 10 feet, together with such other data as may be of value.

SAMPLE NO. 1.

This was taken from the nitrogen plats of the five-year rotation experiments at Wooster, Ohio. The soil is a yellow somewhat sandy clay, lying upon the upper rocks of the Waverly series. It is of glacial origin, but is largely modified by the soft sandy shales upon which it lies, and which have been ground up and mixed with material derived from granite and limestone to the northward. The native rock is abundantly streaked with iron, and a liberal percentage of iron is found in the soil.

The original forest growth of this region was chiefly white oak, with a little admixture of red, scarlet, and black oaks, and an occasional chestnut. The most striking arboreal feature is the thick undergrowth of dogwood.

The topography of the country is rolling, owing entirely to erosion, as the rocks lie in level strata. When the forest was cleared away, the slowly decaying roots of the deep-rooted white oak furnished channels of drainage through the thin sheet of clay to the loosely stratified rocks below, and through their rifts and seams the drainage waters percolated to feed the multitude of springs for which the region is famous. But as the roots decayed more completely the plow and the tramping of teams and pastured stock obliterated these natural channels and artificial drainage became necessary.

The following tables exhibit the results of analyses of this soil:[a]

TABLE I.—*Mechanical analysis of soil from Wooster, Ohio.*

Constituent.	Size of particles.	First 6 inches.
	Millimeters.	*Per cent.*
Gravel	2 to 1	0.56
Coarse sand	1 to 0.5	.86
Medium sand	0.5 to 0.25	.71
Fine sand	0.25 to 0.1	1.79
Very fine sand	0.1 to 0.05	20.47
Silt	0.05 to 0.01	29.97
Fine silt	0.01 to 0.005	36.07
Clay	0.005 to 0.0001	4.74

[a] Ohio Agr. Expt. Sta. Bul. 110.

TABLE II.—*Chemical analysis (1.115 HCl) of soil from Wooster, Ohio.*

Constituent.	First 6 inches.	Second 6 inches.	Third 6 inches.
	Per cent.	*Per cent.*	*Per cent.*
Insoluble	88.71	87.64	88.17
Potassium oxid (K_2O)	.22	.28	.25
Sodium oxid (Na_2O)	.39	.38	.39
Calcium oxid (CaO)	.32	.31	.31
Magnesium oxid (MgO)	.36	.35	.36
Ferric oxid (Fe_2O_3)	2.64	3.29	2.97
Aluminum oxid (Al_2O_3)	2.53	3.49	3.01
Phosphoric acid (P_2O_5)	.80	.80	.80
Sulphuric acid (SO_3)	.04	.05	.05
Loss on ignition	4.48	4.03	4.25

The experiments on this land were commenced in 1888. Dissolved boneblack and dissolved rock have been used as the standard carriers of phosphoric acid; muriate of potash as the source of potash; and nitrate of soda furnished the standard for nitrogen. Where phosphates have been applied it has been at the rate per acre of 320 pounds; muriate of potash at the rate of 260 pounds; nitrate of soda, 440 pounds; and dried blood, 40 pounds, during a five-year rotation.

Incidentally it may be said that nitrogen or potash alone or together have not been profitable, and where ammonium sulphate is the carrier of nitrogen the yields have been smaller than with sodium nitrate.

SAMPLE NO. 2.

This sample is from plat No. 6 (muriate of potash and dried blood plat) of the rotation experiments of the Pennsylvania experiment station. The soil is a magnesium limestone clay loam, about 8 inches in depth, through which fragments of flint are scattered. It has good natural drainage and contains a fair supply of organic matter. The surface soil is fairly uniform in depth and fertility, but the subsoil varies greatly in depth.

The fertilizers are applied twice during the rotation—to the corn and to the wheat—at the rate of 218 and 250 pounds dried blood, 250 pounds dissolved boneblack, and 200 pounds muriate of potash per acre.

Applications of lime have reduced the yields decidedly, while sulphate of ammonia has given greater yields than nitrate of soda.

SAMPLES NOS. 3 AND 4.

These samples are from plats Nos. 10 and 11 of the phosphoric acid experiments at the Maryland station. The soil is a rather stiff clay, naturally quite well drained, though quite level. In general character the plats are quite uniform, in fact more so than most pieces of like area in this formation. The history of the cropping of the land used for this test was, so far as known, as follows: There was a poor stand of grass and weeds on this land in 1888, which was plowed down and seeded to wheat, which was harvested in 1889; grass, 1890–91; corn, 1892; fallowed 1893; wheat, 1894. Clover and timothy were sown in the wheat and gave a good stand. It was limed at the rate of 30 bushels of stone lime per acre in 1893. Since the beginning of the experiments in 1895, muriate of potash and nitrate of soda have been applied in like amounts to all plats, while the source of the phosphoric acid has been varied. Sample No. 3 has not received phosphates since 1880, while sample No. 4 has received in five applications, ground raw S. C. rock at the rate of a total of 2,650 pounds per acre.

SAMPLE NO. 5.

Sample No. 5, from Amherst, Mass., is furnished by the Massachusetts agricultural experiment station from plat O, field F; a friable loam, with a retentive subsoil of clay that is nearly filled with gravel and small stones in the lower strata. Previous to 1887 the field had been used as a meadow and was well worn-out, at that time yielding but a scanty crop of English hay.

The plat (No. 5) in proximity to the one from which the sample was taken, and with which comparisons will be made later, received the following treatment: In 1887 the sod was turned under. The crops grown in 1888, and in succession since, have been Hungarian grass, forage crops, potatoes, wheat, serradella, maize, barley, rye, soy beans, Swedish turnips, and maize. The fertilization began in 1890 with about 500 pounds of dissolved boneblack, 290 pounds of nitrate of soda, and 390 pounds of potash-magnesium sulphate. This application was made yearly till 1895, after which time no more phosphoric acid was added, but the yearly addition of the other ingredients was increased one-half. In 1893 and thereafter the same crops were grown upon the plat (No. 0) from which the sample of soil was secured as upon the above-mentioned one, but the first addition of fertilizer was made in 1896, since which the application of nitrogen and potash has corresponded with that on the other plat. So far as is known, no phosphate has ever been added to plat 0. Both plats were limed at the rate of a ton of quicklime per acre in the spring of 1898. It will be seen that, during 1896, 1897, and 1898, the fertilization of the two plats was the same, but previous to these years plat 0 had received no fertilizer, while plat 5, during a series of years, had received a total application of about 1,900 pounds of nitrate of soda per acre, 2,500 pounds of potash-magnesium sulphate, and 2,500 pounds of dissolved boneblack.

SAMPLE NO. 6.

Sample No. 6 is from plat No. 1 wheat acre of the Kentucky station. Soil is derived from the Lower Silurian limestone, rich in phosphoric acid. The top soil is a brown clayey loam; the subsoil, a yellow clay so retentive as to cause the land to be deficient in natural drainage; the surface soil, 8 to 12 inches deep. It has been in wheat continuously since 1887 without fertilizer of any kind. The soil of the plat does not now produce a crop of wheat. It is of the same character as that of the corn acre, and the data given in regard to it will apply as well to the soil of the corn acre.

SAMPLE NO. 7.

This sample is from plat No. 4 (nitrogen and phosphoric acid plat) of the "soil-test" experiment of the Rhode Island station.

The soil here mentioned is from the "plain." It is of a dark chocolate color, about 4 inches deep, underlaid by an impure clay resting upon gravel and pebbles of unknown depth, which form a good natural drainage. The soil is evidently derived from gneiss, consisting of quartz, orthoclase, and biotite, and made up of glacial drift.

Mechanical analysis.[a]

	Per cent.		Per cent.
Moisture in air-dried sample	1.90	Fine sand, 0.25–0.1 mm	6.66
Organic matter	8.46	Very fine sand, 0.1–0.05 mm	31.65
Gravel, 2–1 mm	1.82	Silt, 0.05–0.01 mm	29.69
Coarse sand, 1–0.05 mm	3.40	Fine silt, 0.01–0.005 mm	4.38
Medium sand, 0.5–0.25 mm	7.82	Clay, 0.005–0.0001 mm	4.81

[a] Rhode Island Agr. Expt. Sta. Bul. 28.

Chemical analysis of air-dried fine soil.[a]

	Per cent.		Per cent.
Insoluble matter	80.632	P_2O_5	0.127
K_2O	.155	Moisture and organic matter	7.888
CaO	.569	Humus	2.752
MgO	.209	Ash from humus	.605
Fe_2O_3	3.463	P_2O_5 in humous ash	.042
Al_2O_3	4.641		

It was found[b] that the amount of phosphoric acid extracted from these soils, rich in organic matter, was increased 41 per cent by substituting the Goss for the above method.

Soil taken from different portions of the same field in 1895 contained, on a water-free basis, humus, 3.86 per cent (by the Huston method, which gives higher results than the Hilgard method, in most cases); humous nitrogen, 0.13 per cent; and free humic acid,[c] 1.52 per cent (Rhode Island station). Soil which had been exhausted of its available potash by fertilization with nitrogen and phosphoric acid, taken from the same field in 1897, yielded only 0.020 per cent of lime by treatment with carbonated water.[d] The soils under discussion give an acid reaction to litmus paper, and fail to produce satisfactory yields in the case of many crops without an addition of lime or other alkaline materials to correct the existing acidity.

In 1890 an experiment was begun with maize to indicate the relative amounts of more active nitrogen, phosphoric acid, and potash within the soil. Previous to this time grass had been growing for many years without fertilization, and hardly enough was produced at the time the experiment began to pay for cutting. In 1890 and 1891 nitrate of soda, 150 pounds; dissolved boneblack, 350 pounds; and muriate of potash, 150 pounds per acre were applied. In 1892 and subsequently the annual application was increased to 480, 600, and 200 pounds, respectively. In 1896 air-slacked lime was applied to all plats at the rate of $2\frac{1}{2}$ tons per acre.

A plat to which a complete fertilizer was applied was not included in this experiment until 1899.

SAMPLE NO. 8.

This soil is from plat No. 67 of the limed series, phosphoric acid experiments, Rhode Island station. No phosphoric acid has been added to this plat.

This land is of the same general character as No. 7. In this experiment there are two series of plats on which the comparative value of different phosphates is being studied. One series is limed, the other is unlimed. Each plat, except the check plats, received, in the course of each year from 1895 to 1899, inclusive, like amounts of phosphoric acid, irrespective of the form. All have received like amounts of nitrate of soda and of muriate of potash. Owing to the very acid character of this soil, which vitiates the results obtained with some of the crops raised, it has been thought best to give the increase due to phosphoric acid of slag meal as well as from the standard phosphoric acid carrier, dissolved phosphate rock.

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[a] Rhode Island Agr. Expt. Sta. Bul 28. Collected 1892. Hilgard method.

[b] U. S. Dept. Agr., Division of Chemistry, Bul. 47.

[c] Method given in Wiley's Agricultural Analysis, vol. 1, p. 331.

[d] U. S. Dept. Agr., Division of Chemistry, Bul. 56.

CHARACTER OF SAMPLES AS INDICATED BY CROPS GROWN.

The data compiled in Table III show the increase in the crops obtained by adding plant foods to the various soils of which these samples are representative:

TABLE III.—*Increase in crops per acre due to plant food added to soils from which samples were taken.*

Soil sample No.	Plant food added.	Wheat.		Oats.		Corn.		Hay.	Barley.	
		Grain.	Straw.	Grain.	Straw.	Grain.	Stover.		Grain.	Straw.
		Lbs.	*Lbs.*	*Lbs.*	*Lbs.*	*Lbs.*	*Lbs.*	*Lbs.*	*Lbs.*	*Lbs.*
1	K_2O	252	507	147	(*b*)	75	106	106	.....	.....
	P_2O_5	571	1,163	387	557	646	162	598	.....	.....
2	K_2O	264	762	77	163	369	1,732	171	.....	.....
	P_2O_5	480	1,167	134	165	717	1,629	817	.....	.....
3	P_2O_5	546	1,411	.....	.....	478	393	375	.....	.....
4*a*	P_2O_5	.....	.....	.....	.....	.....	.....	.....	.....	.....
5	P_2O_5	.....	.....	269	131	3,490	1,360	.....	726	1,890
6	K_2O	135	.....	.....	.....	3,609		.....	.....	.....
	P_2O_5	160	.....	.....	.....	(*b*)	(*b*)	.....	.....	.....
7	K_2O	.....	.....	.....	.....	330	1,320	.....	.....	.....
	P_2O_5	.....	.....	.....	.....	(*b*)	(*b*)	.....	.....	.....
8	P_2O_5, *c* unlimed	.....	.....	787	5,112	1,041	2,159	1,601	.....	.....
	P_2O_5, *c* limed	.....	.....	575	1,725	295	885	1,117	.....	.....
	P_2O_5, *d* unlimed	.....	.....	562	2,437	961	1,853	2,661	.....	.....
	P_2O_5, *d* limed	.....	.....	472	2,097	458	891	1,166	.....	.....

Soil sample No.	Plant food added.	Rye.	Cabbage.	Turnips.	Soy beans.		Potatoes.	Tobacco.	Crimson clover.	Beets.
					Beans.	Straw.				
		Lbs.	*Lbs.*	*Lbs.*	*Lbs.*	*Lbs.*	*Lbs.*	*Lbs.*	*Lbs.*	*Bush.*
5	P_2O_5	1,330	983	574	950	1,360	.....	.....	.....	.....
6	K_2O	.....	.....	.....	.....	.....	5,280	268	.....	.....
	P_2O_5	.....	.....	.....	.....	.....	2,100	142	.....	.....
7	K_2O	.....	.....	.....	.....	.....	2,814	.....	.....	.....
	P_2O_5	.....	.....	.....	.....	.....	2,406	.....	.....	.....
8	P_2O_5, *c* unlimed	.....	.....	320	.....	.....	11,070	.....	4,960	9.5
	P_2O_5, limed	.....	.....	3,665	.....	.....	6,900	.....	460	70
	P_2O_5, *d* unlimed	.....	.....	522	.....	.....	9,900	.....	6,840	154
	P_2O_5, *d* limed	.....	.....	6,335	.....	.....	5,640	.....	820	473

a Fertilized with ground raw phosphate rock and well supplied with available P_2O_5.
b Larger yields without P_2O_5.
c From dissolved South Carolina rock.
d From slag meal.

From the preceding figures we see that—

Sample No. 1 is very deficient in available phosphoric acid for hay, wheat, oats, and corn. The increased yield of oats and wheat due to use of potash is about half that due to phosphoric acid; with corn and hay it is practically nothing.

Sample No. 2 is very deficient in available phosphoric acid for corn, wheat, grass, and oats, being about like No. 1 in this particular. It is deficient in available potash for corn and wheat, but practically not deficient for grass and oats.

Sample No. 3 is about as deficient in phosphoric acid as No. 1 for wheat, corn, and hay.

Sample No 4 has had only ground raw phosphatic rock applied to it, but experiments for five years with crops show that larger yields have been obtained with insoluble phosphate than with soluble or reverted; hence sample No. 4 should be higher in available phosphoric acid than No. 3.

Sample No. 5 is decidedly deficient in phosphoric acid for corn, soy beans, barley, rye, cabbage, turnips, and oats. Particularly so for corn, barley, rye, and soy beans.

Sample No. 6 has never been found to need phosphates, except for potatoes. It is very deficient in available potash for potatoes and corn, somewhat deficient for tobacco, and but little for wheat.

Sample No. 7 is deficient in available potash for potatoes, less deficient for corn; deficient in phosphoric acid for potatoes, but not for corn.

Sample No. 8. is very deficient in available phosphoric acid for potatoes, crimson clover, corn, hay, oats, beets, and turnips; in all cases, except with turnips, much less deficient when limed.

Results of Work on Samples.

Determination of phosphoric acid was asked for in samples Nos. 1, 2, 3, 4, 5, and 8. Determination of potash was asked for in samples Nos. 6 and 7.

CHEMICAL ANALYSES.

The results reported are given in the following table:

Table IV.—*Determinations of potash and phosphoric acid by the N/200 hydrochloric acid method.*

[Parts per million.]

Analyst.	Constituent.	Sample No. 1.	Sample No. 2.	Sample No. 3.	Sample No. 4.	Sample No. 5.	Sample No. 6.	Sample No. 7.	Sample No. 8.
C. C. Moore, Bureau of Chemistry (not corrected for basicity).	Potash	52.0	94.0	136.0	50.0	177.0	16.0	11.0	39.0
	Phosphoric acid	.66	1.3	10.0	6.0	0.66	4.0	1.0	1.0
C. C. Moore, Bureau of Chemistry (corrected for basicity).	Phosphoric acid	.7	1.7	12.0	8.0	.70	4.5	1.0	1.0
F. P. Veitch, Bureau of Soils (not corrected for basicity).	Potash	55.0	111.0	142.0	42.0	175.0	18.0	12.0	42.0
	Phosphoric acid	.6	1.2	11.0	7.0	.5	4.0	2.0	1.6

With regard to phosphoric acid we see that samples Nos. 1, 2, and 8, which are low in available phosphoric acid, show less than 2 parts per million, while No. 3, which is also low, shows from 10 to 11 parts, and No. 7, which should be well supplied with available phosphoric acid, shows only from 1 to 2 parts per million. The results on Nos. 3 and 4 are contrary to the crop history of the soils. The other results are in harmony with their crop history.

With regard to potash, Nos. 6 and 7, which are markedly deficient, show but small amounts dissolved by this method, while No. 1, which is somewhat deficient in available potash, shows 52 to 55 parts per million, more than No. 4 or No. 8, which are presumably well supplied. In view of the fact that the samples represent but a fraction of the feeding depth of plants in these soils, it seems advisable to give the method further trial on samples so taken as to represent approximately the feeding ground of plants.

It seems to the referee that in the use of these methods which remove so little from the soil it is particularly necessary to know the solubility of the plant foods to the full feeding depth of the plants. While the advisability of this was recognized, it was not possible to take the matter up this year.

MECHANICAL ANALYSIS.

In the matter of the advisability of the association's adopting methods for the mechanical analysis of soils, the following self-explanatory correspondence is submitted:

September 12, 1902.

Prof. Milton Whitney,
Chief of Bureau of Soils, Washington, D. C.

Dear Sir: Among the questions referred by the Association of Agricultural Chemists to the referee on soils was that of the importance of the mechanical analysis of soils and the advisability of the association providing in its published methods for mechanical as well as for chemical methods for soil analysis. It seems to the referee that you are the one who is best fitted to make a statement covering these points, and he therefore respectfully asks that you write a letter to be submitted over your signature as part of the report on soils, stating to what extent the physical condition of a soil as revealed by its mechanical analysis may be regarded as exerting a measurable or practical effect on the fertility or crop-producing power of that soil.

Your discussion of the advisability of changing the present limits of size for the several separates obtained by the standard mechanical method, and of the closeness with which results can be duplicated by the same and by different workers, will also be appreciated.

Yours, very respectfully,

F. P. Veitch,
Referee on Soils.

September 30, 1902.

Mr. F. P. Veitch,
Referee on Soils, Bureau of Soils:

Sir: Your letter of September 12 has been received, referring to the advisability of the Association of Official Agricultural Chemists providing in its published methods for mechanical as well as for chemical methods for soil analysis. This letter has been given full and careful consideration, and I find it a rather difficult question to deal with, as there are so many contingencies that have to be taken into account, which I realize it is difficult for the analyst to inform himself upon and to consider in the examination of individual samples.

Generally speaking, I believe the mechanical analysis throws an important light upon the character of the soil and the character of the crop to which it is adapted, but, as in the chemical analysis, there are questions of climate, physiography, transportation, and markets, as well as other more subtle differences in the structure of soil which have to be given full consideration in using the results of the mechanical analysis.

To reply first to your last inquiry, I think it very undesirable to have a large number of physical separations, as it is impossible for us to use many of these separations in our estimate of the physical properties or the physical character of the soil. As you know, we have adopted seven separations: (1) Fine gravel, (2) coarse sand, (3) medium sand, (4) fine sand, (5) very fine sand, (6) silt, and (7) clay. I think that these various grades should stand, as these differences can be recognized in the field by our soil experts, and it is quite clearly recognized that these several separations occurring in different proportions in the soil, influence in a more or less marked manner the character of the crop adapted to the land, its relation to drainage and agricultural practice. In the correlation of soils into great classes in this Bureau, we are, however, reducing these separations to four principal groups by combining the fine gravel, coarse sand, and medium sand into what we roughly designate as "coarse grades;" the fine sand and the very fine sand into what we roughly consider "fine sand material;" the silt, which has in the field peculiar properties typically shown in a true loess, and clay, which has certain characteristic properties of plasticity, which, however, may be shown by any of the other groups.

It is useful in comparing, for example, the Cecil clay and the Hagerstown clay, or the Cecil sandy loam, the Cecil loam, and the Cecil clay, to see from this abbreviated statement of the results of the mechanical analysis whether the coarse sand, fine sand, or the silt, or the clay predominates, or what the relation between these different grades bear to each other in the different soils or different groups of soils.

The practice of the Bureau has been to simplify, as much as possible, the broad classification of the soils, and for this purpose 16 general classes have been established, viz, stony loam, gravel, gravelly loam, dune sand, sand, fine sand, sandy loam, fine sandy loam, loam, shale loam, silt loam, clay loam, clay, adobe, meadow, and muck and swamp. We endeavor to indicate in the type name that the soil may be thrown into one or another of these general classes, but each one of these classes may contain any number of different types of soils so long as their individual characters and peculiarities are clearly stated.

Furthermore, we have decided, after full and careful consideration, that these classes shall be based upon the field judgment of the men rather than upon the mechanical

analysis. It is quite possible that a soil will show from the mechanical analysis 60 or 70 per cent of silt, which would indicate that it belonged to the loess type, and should be called a silt loam, while the properties in the field show it to be a true clay in being extremely plastic and impervious to water and possessing none of the friable properties of a loess. Again, we may have a soil which shows a low content of clay with a high content of fine sand, having in the field an impervious character, high retentive properties for water, and being more or less plastic, in which case the soil would go under the general class of a clay soil regardless of the fact that the mechanical analysis shows the soil to contain relatively little clay.

While these differences may be perplexing to the person who is classifying the results of the laboratory work, they are nevertheless valuable in pointing out essential properties of the soil, which would otherwise be overlooked. A soil containing 70 per cent of silt, but having the properties in the field of a true clay, is interesting from the standpoint of the soil physicist in indicating certain properties the soil possesses differing markedly from a loess containing 70 per cent of silt, and, furthermore, these differences unquestionably give valuable guides as to the proper treatment of these soils, which would not be deduced alone from the mechanical analysis or from the field examination.

If a soil is described as a sandy soil or a sandy loam and the mechanical analysis shows that it contains not to exceed 6 or 8 per cent of clay, I should have no hesitation in stating that early truck crops could be produced on the soil; but whether it would be an economic venture to develop the industry would depend upon climatic conditions, transportation facilities, and market demands. If the soil contains 10 per cent and over I should say that it would be adapted to a different class of truck crops, particularly to the late varieties of potatoes and to the heavy truck crops, such as cabbage. If the soil contains 15 per cent of clay, I should say that it would be unwise to expect any successful development in early truck crops, although it might be admirably adapted to market gardening which could be carried on within hauling distance of a city or town.

With the knowledge we now possess of the influence of the soil upon the commercial type of tobacco, it should be possible, from the mechanical analysis alone, within certain prescribed limits which mark our different tobacco districts, to determine the character of the leaf that would be produced: In the Northern cigar-tobacco districts, whether a wrapper, binder, or filler could be produced on a soil of any given texture; in the Southern districts, whether a bright tobacco, manufacturing tobacco, or the different types of export tobacco could be produced. But it would be unwise to predict either success or failure from similar analyses of soils taken outside of the present recognized tobacco districts. The commercial type of tobacco is so markedly influenced by the physical character of the soil that, in this particular case, as no doubt with many other crops, the commercial type is dependent upon this character, with little, if any, regard to the actual chemical composition of the soil. The chemical composition of the soil undoubtedly influences the yield and quality of crops under these conditions, but it has little noticeable effect upon the type of tobacco which is grown. In other words, the yield, size of leaf, burn, and grain of the leaf can undoubtedly be modified by fertilization, but so far as my experience goes fertilization can not produce a wrapper leaf on a filler soil, as these types are dependent primarily under given climatic conditions upon the texture and physical properties of the soils. Similar relations could be shown between other crops and the physical character of the soil, but it would hardly be justified in the limits of such a brief communication as is probably expected in reply to your letter.

As the operations of the Bureau of Soils extends over wider areas of the country, resulting in the establishment of recognized types and reports as to the relation of these types to crops, it is believed that a basis will be given for the correlation of soils even outside of the areas which have been surveyed and which will make it imperative for the agricultural chemist to adopt methods of mechanical analysis in conjunction with his chemical work in showing the class of crops adapted to the soil in addition to his chemical work which may show the relation of the soil to the actual yield of crops. I consider it inadvisable to increase the number of separations beyond the seven grades which we now recognize. The actual size or limits of these separations is a relatively unimportant matter. It is necessarily an arbitrary measure. Whether the conventional separation in use by the Bureau is adopted or whether the separations vary according to the square root of 10 or some other mathematical relation is unimportant, except for the fact that this Bureau has unquestionably the largest and most representative collection of soil samples that has ever been made, and has made and published upward of 3,000 analyses covering all of the most important types of soil in this country and many from abroad. Furthermore, the

soil survey has been extended to 30 States in this country and is rapidly being extended in an immeasurably greater scope than can be given by any individual or State. It would, therefore, seem advisable for the analyst, in view of the work thus far done, and the enormous extension of this work which will undoubtedly be made possible through the liberal appropriations by Congress, to adopt the same separations as are here used. This would insure a uniformity of results. It would make possible a correlation of samples with areas which have been accurately mapped and carefully investigated by this Bureau, and would, in my judgment, add greatly to the value of the work of the individual analyst in comparison with what could be accomplished by a change in the limits of size of the separation at this time by any individual or by any association.

Careful watch has been kept upon the accuracy of the details of the method as shown by duplicate analyses by the same and different individuals in this Bureau, and it is my judgment that the limit of error is much smaller than the justifiable phases which are recognized by our field men, or than we are able to recognize in their effect upon the crop. In a truck soil containing not to exceed 8 per cent of clay, I can see no advantage in working for results closer than 1 or 2 per cent of clay. A difference of half of 1 per cent has no meaning to me. Samples from different parts of the type may differ much more than this with no apparent difference in their relations to crops, and if duplicate results by different workers come within 1 or 2 per cent of the amount of clay in such a soil, it would be perfectly satisfactory to me. On the other hand, in a clay soil the difference between 30 and 35 per cent of clay is unimportant, as I think we can not recognize such differences in crop relations. Again, 50 per cent of silt with certain physical properties places a soil in the class of loess soils. I would not recognize any essential difference in such a type if duplicate analyses or duplicate samples showed 60 per cent of silt, because, in my judgment, the difference between 50 per cent and 60 per cent of silt would not have so marked an effect upon the crop as to be readily recognized. It would certainly be far less liable to affect the crop than would different methods of cultivation. If there was 70 or 80 per cent of silt, this would be a different matter from the case of a soil containing 50 per cent of silt, such as we have just been considering, and I should expect different crop relations and look for different cultural methods as desirable. While I would not advocate any less care in the mechanical analyses than is now given, I feel satisfied that the methods at present used are accurate far within the limits of variation which may be allowed in any type of soil, and far within the limits of variation of the effect of the soil on the crop. We must not forget that while we want accuracy in our laboratory work, there must always be considerable variation in the limits of our field classification, for there are many questions, such as climate, physiography, drainage, and farm practice, which are recognized as having large influences upon crop production which can not be recognized in a statement of a mechanical analysis. Considerable variation, therefore, may be allowed in the mechanical analysis of soils within the same type from which the same results may be attained, both as to character and yield of crops.

Very truly, yours,

Milton Whitney,
Chief Bureau of Soils.

The referee would merely add to this, that whoever attempts to determine the availability of plant food, or the crop-producing power of soils, be he chemist, soil physicist, or agronomist, needs all the data he can get; and if the chemist is going to attempt to say what a soil will do, or how it can be most economically improved, he should have methods for making the physical as well as the chemical examination.

Methods for the Analysis of Alkali Soils.

The points which have received attention are the effect of dilution on the amount of salt dissolved, and the titration methods for the determination of carbonates, bicarbonates, and chlorids. As our present methods for the determination of silica, sulphuric acid, and the bases are applicable here, no attention was given to these points. For this work 10 samples of alkali soils and crusts were selected, and prepared for analysis by passing through a 2-mm sieve. The samples represented soils containing large and small quantities of the acid radicals to be determined, as well as

samples high and also lower in soluble lime compounds. The results obtained are given in the following table:

TABLE V.—*Effect of dilution on solubility of alkali soils in water.*

RESULTS BY J. F. BEAZEALE.

Dilution.	Constituents.	4721.	4724.	4686.	4759.	4889.	5055.	5102.	5103.	6315.	4782.
		Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
50 grams per liter..	Ca.....	0.08	0.08	Trace.	1.65	0.02	0.03	0.25	Trace.	2.26	1.43
	Mg.....	.01	.01	Trace.	.08	Trace.	.01	.36	Trace.	.08	.67
	N.....	.46	1.58	9.39	5.12	22.70	.39	17.66	11.91	1.66	4.03
	K.....	.13	.14	.11	.28	.68	.05	.09	.07	.07	.06
100 grams per liter.	CO_3.....	.....	.03	6.86	.02	13.40	.15	.....	6.00	.....	.....
	HCO_3...	.23	.35	5.45	.05	13.93	.26	.08	3.57	.03	.08
	Cl.....	.47	1.41	1.76	6.29	.91	.35	18.01	3.60	5.54	5.96
	SO_4.....	.22	.76	1.32	3.60	.98	.04	5.14	5.21	.12	3.73
50 grams per liter..	CO_3.....	.03	.07	5.96	.....	13.40	.17	.....	5.84	.....	.....
	HCO_3...	.26	.45	6.85	.12	16.90	.14	.12	3.74	.07	.09
	Cl.....	.44	1.44	1.80	6.48	.84	.34	17.62	2.24	5.36	6.65
	SO_4.....	.19	.63	1.28	4.32	.99	.04	12.80	7.09	.09	5.49
25 grams per liter..	CO_3.....	.07	.07	5.76	.....	12.47	.16	.....	5.96	.....	.....
	HCO_3...	.52	.58	5.28	.17	16.43	.24	.19	3.86	.09	.14
	Cl.....	.50	1.40	1.96	5.34	.84	.34	16.14	2.56	5.22	6.20
	SO_4.....	.27	.77	1.67	6.34	1.12	.09	12.40	7.37	.13	7.06
10 grams per liter..	CO_3.....	.17	.23	6.48	.....	13.00	.59	.....	5.96	.....	.....
	HCO_3...	.72	.90	6.52	.24	15.22	1.20	.18	4.53	.24	.24
	Cl.....	.56	1.75	1.40	6.44	1.00	.35	16.28	2.52	5.47	6.61
	SO_4.....	.27	.70	1.20	9.95	1.04	.04	13.42	8.83	.12	9.11

RESULTS BY F. P. VEITCH.

50 grams per liter..	CO_3.....	0.07	0.12	6.57	0.06	14.54	0.21	.....	6.86	.....	.....
	HCO_3...	.31	.38	6.54	.07	15.26	.02	.12	5.16	.04	.....
	Cl.....	.47	1.51	1.40	5.71	.96	.30	17.04	3.41	5.21	.....
	SO_4.....	.17	.43	{a .89 / a1.40}	a 2.94 / a 4.91	.73	.02	9.03 / a14.60	7.91 / a12.72	.18	.....
10 grams per liter..	CO_3.....	.24	.24	6.91	.....	14.66	.36	.....	6.31	.....	.....
	HCO_3...	.72	.61	5.32	.30	15.22	.86	.30	5.92	.36	.24
	Cl.....	.56	1.40	1.40	5.88	.84	.42	17.20	3.50	5.32	6.56
	SO_4.....	.30	.86	1.39	10.52 / a12.04	1.04	.18	14.64 / a14.38	12.92	.12	10.18

a Determination made after ninety-six hours standing in contact with the soil.

The results may be summed up as follows: The concentration of the solution materially affects the rapidity of solution of sulphates, particularly calcium sulphate, and it is quite evident that equilibrium has not always been reached in twenty-four hours. The chlorin determination is the most satisfactory and appears to be the least affected by the concentration of the solution, while equilibrium is usually reached within the twenty-four hours. The determination of carbonates and of bicarbonates when present in large quantities has not been very satisfactory to the referee. This is attributed to the uncertain end point with phenolphthalein, which is far from sharp, particularly in the colored solutions produced by black alkali. The total titration of carbonates plus bicarbonates, using methyl orange, was somewhat more satisfactory.

While it may be true that the accurate determination of that portion of the soluble salts in excess of the quantity fatal to vegetation may not be of practical value so far as such soils are concerned at the present time, yet the possibility of reclaiming such lands and the importance of the composition of irrigating waters for this purpose make it highly desirable that we have a uniform and reliable method for this work. The referee, therefore, will recommend that this matter go to the referee next year, with the suggestion that the concentration of solution and time required for all salts to come to equilibrium receive further attention. It is to be hoped that those members whose location and work bring them in contact with this class of soils will give the matter some attention.

RECOMMENDATIONS.

It is recommended:

(1) That the N/200 HCl method be given further trial.

(2) That samples be so taken that it will be possible to determine by this method the available potash and phosphoric acid in each 12 or 9 inches to a total depth of 3 or 4 feet.

(3) That the methods for the analysis of alkali soils be referred to the referee with instructions to determine the most desirable amount of soil and the amount of water to be used in dissolving the soluble salts.

The PRESIDENT. If there is no objection the reading of the papers relating to soils will be deferred and we shall have the pleasure of listening to another guest of the association. Some thirteen years ago when I went to Europe it was my great pleasure to make the acquaintance of our highest authority on explosives, and it now gives me particular pleasure to present him in Washington, Professor Munroe, of Columbian University.

ADDRESS OF PROFESSOR MUNROE, OF COLUMBIAN UNIVERSITY.

GENTLEMEN. When I greeted your president and he extended to me an invitation to meet you this morning, my old friend, your honored secretary, informed me that it was the custom to make a speech when introduced, but I can not make a speech. While I feel complimented by being called upon, I am at a loss how to greet you. I would greet you in behalf of the university, but the president has done so in a most interesting manner. I would greet you in behalf of Washington, but there is no reason why I should do that, since Washington is the common home of us all. I have the privilege of being here to a greater extent than you, but Washington is the home of all Americans. I simply greet you as I would at your own home.

I would say that I have been interested in this organization since its beginning and have noticed the steps that were being taken and the great progress made. I feel very much pleased at what it has accomplished. I have been glad to call the attention of my students to the work of the association along the line of agriculture, and have urged them to attend the meetings of this body, to see you in person and to listen to these discussions. The accounts which I have read of these proceedings as I have received them from year to year have been very interesting, and I hope that I may continue to get them.

I have been much interested in your attempt to secure uniformity in methods. Many years ago at Newport, in purchasing materials for the Government, I was obliged to make specifications for them. There was difficulty in securing material to conform to the specifications at that time. Some twenty years ago I suggested that we append to the specifications the method by which the different constituents

called for should be determined. It may be seen that the methods then proposed were not the most exact nor the best, but it was necessary that the analysts should follow the same method. The errors of the methods were eliminated and only the errors of the analysts remained. Your method of examining into the different methods proposed and then declaring that certain methods shall for the time be the official method seems to me to be most admirable. You are ready to change when the better method is proposed and this agreement is a marked progress. In order to obtain certain data it is necessary that you follow similar methods and, even if there is some variation in the data, it is not so unsatisfactory as it otherwise might be.

I repeat that I feel gratified at your having invited me to meet you, and I am glad to say that I shall be able to make another contribution other than the few words I have spoken. Someone has expressed a desire for the bulletin which has been published by the Census Bureau on Chemicals and Allied Products, and, so far as possible, I shall be glad to supply copies to your members. That will be my chemical contribution to this meeting.

The PRESIDENT. I am sure we appreciate the honor of having Professor Munroe with us, and in behalf of the association I extend to him our thanks for the donation of these publications.

REPORT OF COMMITTEE ON NOMINATIONS.

Mr. BIGELOW. We would nominate for vice-president Mr. M. E. Jaffa; for secretary, Mr. H. W. Wiley, and for the additional members of the executive committee, Messrs. Penny and Leitch. The recommendation includes the nomination for president of Mr. Davidson.

Mr. VAN SLYKE. I move that the report of the committee be adopted and that the secretary be instructed to cast the ballot for the officers designated.

The motion was carried and the officers were declared duly elected.

Mr. BIGELOW. I would like to say for the benefit of those who can go to Cabin John that we will be able to get a very nice dinner for $1, but it will not include wine or anything of that nature. I would like to know how many members can go. We will take the cars that pass in front of the Ebbitt House, and it is suggested that we start about 5 o'clock.

A QUANTITATIVE METHOD FOR DETERMINING THE ACIDITY OF SOILS.

By C. G. HOPKINS, W. H. KNOX, and J. H. PETTIT.

Although for many years we have been able to determine by qualitative methods whether a soil is acid, or sour, and although different degrees of acidity have sometimes been recognized and described by such terms as slightly acid, very acid, strongly acid, etc., no practical quantitative method for determining the exact degree of acidity and the consequent quantity of lime required per acre to correct or neutralize the acidity of the soil has been described so far as the authors have been able to learn. Certainly no such method is in common use.

The method which we have worked out is based upon the reaction which occurs when solutions of mineral salts are added to acid soils. The acids of the soils are themselves very difficultly soluble, and it is practically impossible to completely extract them from the soil with distilled water, even though large quantities of

water be percolated through the soil; but, when a mineral salt solution is added to the soil, the acids apparently unite with the mineral base, evidently liberating the mineral acid, or an acid salt which, of course, is perfectly soluble, and whose titrating power furnishes a very satisfactory basis for determining the total acidity of the soil.

For use in quantitative work a 5 per cent solution of commercial sodium chlorid (a good grade of common table salt) has been found to be entirely satisfactory. Of course, other mineral salts, as potassium chlorid, serve the purpose equally well, but they are no better than common salt and are considerably more expensive.

The details of the method are as follows: Place 100 grams of the soil in a stout, medium wide-mouthed bottle of about 400-cc capacity; add a sufficient quantity of a 5 per cent sodium chlorid solution to make 250 cc of liquid, including the moisture contained in the soil, but independent of the volume of the soil itself (the moisture content of thoroughly air-dry soils will not cause an appreciable error, if neglected); close tightly with a rubber stopper; place in a shaking machine, and shake for three hours. (Shaking by hand every half hour for about twelve hours will accomplish the same result). Place the bottle in a suitable centrifuge and whirl till the soil is thrown down sufficiently to allow at least 125 cc of clear liquid to be blown off by means of two glass tubes held in a rubber stopper and arranged about the same as in the ordinary "spritz" bottle, except that the exit tube should be about 2 mm at the end instead of terminating in a fine jet. Instead of using the centrifuge the bottles may be allowed to stand a few hours, or 125 cc of the liquid may be filtered off, care being taken to avoid concentration by evaporation. Exactly 125 cc of the clear liquid (one-half the total volume of liquid) are placed in an Erlenmeyer flask, heated to boiling[a] to expel traces of carbon dioxid and to insure a sharp "end reaction," and then titrated with standard fixed alkali, phenolphthalein being used as the indicator.

The reaction between the soil acids and the sodium chlorid does not run to an end, but it has been found that at the end of three hours' shaking, under the conditions described above, an equilibrium is established, and that no appreciable additional quantity of acid is liberated with repeated or long-continued shaking. In other words, the solution has the same degree of acidity whether the titration is made as soon as possible after the three hours' shaking, or after shaking for three hours it is allowed to stand for twenty-four hours and then again shaken for three hours before drawing off one-half of the solution to titrate. If, however, after the 125 cc of liquid are removed and titrated, an equal quantity of fresh salt solution is added to the residue contained in the shaker bottle, the contents are again shaken for three hours, and 125 cc of the solution is drawn off and titrated, this second titer will be found to be approximately two-thirds of the first titration, instead of one-half of it, as it would be if the reaction had run to an end under the first treatment. If this process is further repeated, the third titration will be found to be about two-thirds of the second, and the fourth to be two-thirds of the third, etc. We are thus able by this fractional process to separate the acid equivalent from the soil to within an indeterminable amount, and the results obtained form a simple descending geometric series, as may be seen from the following data, in which are shown the duplicate readings (in cubic centimeters of standard alkali) of eleven different titrations of the acid obtained in these fractional separations.

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[a] No appreciable quantitity of hydrochloric acid is lost from such dilute solutions even when heated to boiling for a short time.

TABLE I.—*Standard alkali neutralized by successive saline extracts.*

Titration (soil sample No. 1.)	(A) Standard alkali.	(B) Standard alkali.	(Average.) Standard alkali.	Ratio to preceding titration.
	cc.	*cc.*	*cc.*	
First	8.9	9.1	9.0	.....
Second	5.8	5.6	5.7	0.633
Third	3.9	3.5	3.7	.649
Fourth	2.7	2.6	2.65	.716
Fifth	1.9	1.9	1.9	.717
Sixth	1.25	1.25	1.25	.658
Seventh	1.0	1.0	1.0	.800
Eighth	.75	.75	.75	.750
Ninth	.5	.5	.5	.667
Tenth	.3	.3	.3	.600
Eleventh	.2	.2	.2	.667
Average ratio	.....	.....	.....	.686

It will be observed that the ratio is fairly constant, considering the small amounts of liquid measured in the titrations.

The duplicate readings of the first and second titrations on four other samples of soil gave the following results:

TABLE II.—*Comparison of first and second soil extracts.*

Soil sample No.—	First titration.			Second titration.			Ratio of second to first.
	(A) Standard alkali.	(B) Standard alkali.	(Average.) Standard alkali.	(A) Standard alkali.	(B) Standard alkali.	(Average.) Standard alkali.	
	cc.	*cc.*	*cc.*	*cc.*	*cc.*	*cc.*	
2	18.1	18.6	18.35	12.6	12.2	12.4	0.676
...	5.7	5.6	5.65	3.7	3.75	3.73	.660
4	4.8	5.2	5.00	3.0	3.2	3.1	.620
5	2.8	2.8	2.8	1.8	1.9	1.85	.661
Average ratio	.....	.....	.....	.....	.....	.....	.654

If we take an average of these two general averages, we have 0.67, or approximately the fraction $\frac{2}{3}$. We are investigating still further this ratio, or the relation of each titration reading to the preceding one, but tentatively we are using this ratio and believe it is very approximately correct. By computation from these data, it becomes a simple matter to obtain a factor by means of which we can compute the total acidity from the first titration. For example, if we let X equal the constant ratio, S the total acidity, and 1 the first titration, we have the following equation:

$$S=1+X+X^2+X^3+X^4+ \ldots\ldots X^n$$

$$\text{or } S=\frac{1}{1-X}$$

$$\text{If } X=\tfrac{2}{3}, \text{ then } S=\frac{1}{1-\frac{2}{3}}=3.$$

Thus, if $\frac{2}{3}$ is the correct ratio of each titration to the preceding one, then the total acidity of the soil is three times the first titration. From the data which we have thus far obtained, we believe this factor to be very nearly exact; and in practical work we recommend that only the first titration be made as above described and that

this reading be multiplied by the factor 3 to determine the total acidity in the sample of soil taken.[a] If we apply this rule to soil No. 1, we have 26.7 cc and 27.3 cc, or an average of 27 cc, based upon the first titration only; whereas if we add together all titrations and then add to that sum 0.4 cc, or twice the amount of the eleventh titration, we have 27.6 cc and 27.1 cc, or an average of 27.35 cc, based on fractional separations and absolute titration of the total acidity excepting the 0.4 cc in the final residue.

It is convenient to have the strength of the alkali such that 1 cc is equivalent to $3\frac{1}{3}$ mgs of calcium carbonate, so that the number of cubic centimeters of alkali used in the titration corresponds to the number of centigrams of calcium carbonate required to neutralize the acid in 100 grams of the soil sampled. In other words, each cubic centimeter of alkali required for the single titration corresponds to one-hundredth of 1 per cent of the soil in terms of calcium carbonate required By computation from this datum and from the apparent specific gravity of the soil, as used in the determination, and the thickness of the stratum sampled, the exact amount of calcium carbonate required to correct the acidity of the soil is readily determined; and 56 per cent of this amount gives the quantity of fresh burned lime required, in case it is desired to use this form of lime.

If we can make our titration exact to one-tenth of a cubic centimeter of the standard alkali, which corresponds to one-thousandth of 1 per cent of calcium carbonate required by the soil to neutralize its acidity, the limit of error, or perhaps we might better say, the limit of accuracy, is 3 pounds of calcium carbonate per acre-inch of soil or 36 pounds per acre-foot, on the basis of 3,600,000 pounds of soil to the acre-foot; and we can compute the amount required by 40 acre-inches, or by an acre-meter, if we may use the term, to within a limit of error of 120 pounds of calcium carbonate or 70 pounds of lime.

To indicate the ease and rapidity of manipulation of this method, it may be said that with the shaking machine which we are using and without the use of a centrifuge, one analyst can easily determine quantitatively, and in duplicate, the degree of acidity in 30 different samples of soil in one day.

That the quantitative determination of the lime required by soils is of great practical significance, is evidenced by the fact that we find exceedingly marked differences in the needs of different soils, as may be seen from the following tabular statement:

TABLE III.—*Data employed in the determination of the acidity or lime requirement of soils.*

Field or plot tested	Name of stratum sampled.	Location of stratum.	Apparent specific gravity of soil.	Weight of stratum per acre.	Alkali required for the titration.		$CaCO_3$ required by soil.	$CaCO_3$ required for stratum per acre.
		Inches.		*Pounds.*	*cc.*	*cc.*	*Per cent.*	*Pounds.*
A	Surface	0–6	1.326	1,798,000	1.9	1.7	0.018	324
	Subsurface	6–19	1.349	3,963,000	7.2	7.2	.072	2,853
	Subsoil	19–40	1.456	6,910,000	14.4	14.7	.146	10,088
B	Surface	0–7	.726	1,149,000	1.7	1.7	.017	195
	Subsurface	7–17.5	1.278	3,032,000	.....	.....	.....	.....
	Subsoil	17.5–40	1.299	6,605,000	.....	.....	.....	.....
C	Surface	0–5	1.227	1,387,000	8.7	8.5	.086	1,193
	Subsurface	5–20.5	1.256	4,400,000	11.7	11.9	.118	5,192
	Subsoil	20.5–40	1.354	5,967,000	31.1	31.3	.312	18,617

[a] Since this paper was read some additional data have been obtained which show that the factor 3 is too small. Further results will be offered for publication within a short time. In practical work we now advise using the factor 4, which will probably prove to be above the exact figure, but in practice it is advisable to apply at least a small excess of lime above the actual present requirements of the soil.—C. G. HOPKINS.

TABLE III.—*Data employed in the determination of the acidity or lime requirement of soils*—Continued.

Field or plot tested.	Name of stratum sampled.	Location of stratum.	Apparent specific gravity of soil.	Weight of stratum per acre.	Alkali required for the titration.		$CaCO_3$ required by soil.	$CaCO_3$ required for stratum per acre.
		Inches.		*Pounds.*	*cc.*	*cc.*	*Per cent.*	*Pounds.*
D	Surface	0–6	1.291	1,751,000	0.6	0.6	0.006	105
	Subsurface	6–24	1.315	5,349,000	.3	.4	.004	214
	Subsoil	24–40	1.328	4,802,000	1.9	1.9	.019	912
E	Surface	0–7	1.307	2,068,000	.6	.6	.006	124
	Subsurface	7–17	1.368	3,092,000	.3	.3	.003	93
	Subsoil	17–40	1.408	7,319,000				
F	Surface	0–7	1.238	1,958,000	6.6	6.8	.067	1,312
	Subsurface	7–16	1.256	2,554,000	14.9	14.9	.149	3,806
	Subsoil	16–42	1.364	8,012,000	9.3	9.5	.094	7,531
	Lower subsoil	42–54	1.357	3,679,000	.1	.1	.001	37

It will be observed that some soils are exceedingly acid, and that they will require exceedingly heavy applications of some form of lime to produce a neutral condition. The soil in field A requires 324 pounds of calcium carbonate per acre to neutralize the surface, or plowed soil; 2,853 pounds to neutralize the subsurface, or that which lies between the plow line and the subsoil line, and 10,088 pounds to correct the acidity of the subsoil to a depth of 40 inches. The total amount required by this soil to neutralize the acidity to a depth of 40 inches is 13,265 pounds of calcium carbonate, or about 6½ tons. This is equivalent to about 3½ tons of burned lime.

It should be stated that we do not know as yet to what depth it is necessary to neutralize the soil acidity. We hope to have some definite information on this point within a few years. It is certainly safe to say that the acidity of the plowed soil should be corrected, and it seems very probable that it will be advantageous to apply some excess above what is required for that purpose. We are carrying on some experiments to determine how rapidly lime is carried into the lower depths of the soil; or, in other words, how much time will be required before lime which is mixed with the surface soil will begin to reduce the acidity of the subsurface or subsoil.

The soil of field B is very slightly acid, the total amount of calcium carbonate required being only 195 pounds per acre, and this is all needed in the surface soil. Indeed, both the subsurface and subsoil of this field were found to contain lime carbonate, and all that is needed to correct the slight acidity of the surface soil is somewhat deeper plowing than has been practiced heretofore.

Field C is possessed of one of the most acid soils which we have found in the course of several hundred examinations of acid soils. The plowed soil requires 1,193 pounds and the subsurface 5,192, while to correct the total acidity of this soil to a depth of 40 inches requires 25,000 pounds, or 12½ tons of calcium carbonate, equivalent to 7 tons of burned lime.

Field D possesses a rather small degree of acidity, 1,231 pounds of calcium carbonate, or 689 pounds of burned lime, being sufficient to neutralize the soil acidity to a depth of 40 inches.

Field E requires a total of only 217 pounds of calcium carbonate. The subsoil was found not only free from acidity, but it contains abundance of calcium carbonate to correct the acidity of the upper strata; but, as there is no practical method of effecting such a translocation, it is necessary to apply some form of lime to the surface.

It will be noted that there are not only marked differences in the degree of acidity of acid soils, but the acidity of distinctly acid soils is markedly different in different

strata of the same soil; and, furthermore, the acidity increases with depth in some soils and decreases in others, while in field F the acidity increases from the surface to the subsurface, and then grows less in the ordinary subsoil, practically disappearing in the lower subsoil below 42 inches. This condition is probably explained by the fact that the subsoil stratum lying between 16 and 42 inches in depth is of a stiff clayey nature and nearly impervious to water, and the soil acids of the upper strata have not been carried through it to any appreciable extent. This field requires a total of 12,686 pounds of calcium carbonate, or 7,104 pounds of burned lime, to correct the acidity of the soil, and it may be noted that this applies to the total depth of the soil in this field.

It may be pointed out that there are several advantages of considerable economic value in being able to apply lime quantitatively in correcting the acidity of soils; among these advantages may be mentioned the following:

1. One may be sure that he is applying sufficient lime to correct the acidity and thus really benefit the soil.

2. One may avoid a large waste of lime by applying an ample amount without a large excess.

3. One may correct the acidity of the soil without danger of the possible injury to the land which is thought to be sometimes produced by excessive applications of caustic lime.

In our own work we already have illustrations of some of these advantages. For example, an application of only 320 pounds per acre of air-slacked lime to a very slightly acid soil effected an increase of more than one-half ton of air-dry alfalfa hay per acre for each of the first two cuttings this season, while somewhat heavier but nevertheless insufficient applications on exceedingly acid soils have produced no apparent benefit, and, in fact, have led people who are not cognizant of the strongly acid character of the soil, to suppose that the soil does not need lime.

In conclusion, it is desired to state that this method of making quantitative determinations of the acidity or lime requirement of soils has now been in almost constant use for nearly a year in the laboratories of the University of Illinois Agricultural Experiment Station. Quantitative applications of lime have been made to soils in the laboratory in accordance with the determinations made by this method, and the acidity of the soil has been found to have been practically neutralized. The method has been applied to pot-culture investigations and also to field experiments on a large scale, involving carloads of the material, and it is asserted with confidence that it can be relied upon to give trustworthy results. A brief description of this method was given before the Illinois Farmers' Institute in February of the present year. It has also been described to a number of other people interested in the study of soils, including several who are engaged in soil investigations in the United States Department of Agriculture, and it is gratifying to state that it has met with very general approval. The authors beg to report the method to this association with the hope that it may add to the satisfaction and encouragement which we all find in anybody's discovery or development of any method or principle which materially assists in reducing agricultural practice to a scientific basis.

The PRESIDENT. The eyes of this association as well as all those interested in agriculture are always upon the Secretary of Agriculture. From my own knowledge of the work that has been done for the agricultural interests of this country, I would say that no Secretary has ever grasped the situation so completely or has been able to accomplish so much for the agriculture of this country as our present Secretary. It gives me, therefore, the utmost pleasure to introduce to you the honorable Secretary of Agriculture, Mr. James Wilson.

ADDRESS OF SECRETARY WILSON.

Mr. President and Gentlemen of the Association: I came here merely to take off my hat and welcome you to the city, and to congratulate you on the good work you are doing in the interest of our country. There are few people who know how fast the United States is progressing along all scientific lines. I hardly know of anyone who makes a special study of the matter; it keeps me busy to keep up with my own Department. The kind words just spoken by your president concerning myself require a word of explanation. I try to get the right man for the right place, and after I have found that man I take the check line out of the hook and give him a free head and he brings things to pass.

You never had a Secretary who understood all the sciences. One might spend fifty years studying them and then find that he was fifty years behind and that he must begin all over again, and so on until he was too old to learn. I have gotten over the notion that I must understand the details of every scientist's work. I try to study the scientist. I think the Department of Agriculture has as fine a corps of scientists as can be found on the face of the earth. As we progress, grow, and develop in the United States, we need chemists. We are needing them more and more now to safeguard the health of our people, and it is necessary to have their assistance that the people shall not be poisoned and that they shall not be defrauded by the quality of the food they necessarily consume.

The manufacturers' work grows and develops just as fast as the chemists help them along and no faster. For drugs, for example, we are heavily indebted to Europe and pay heavily every year. Scientists of the Department of Agriculture are about to undertake bringing into our country all the drug plants used in the work in chemistry. That will help along this one line. I have one determination which I hold strongly, and that is that whenever I see Uncle Sam paying for anything from foreign countries I want to find out whether that thing can not be produced at home. Four years ago we manufactured from beets 16,000 tons of sugar, the next year 41,000 tons, the year after that 72,000 tons, and the year after that 184,000 tons. This year it will be over 250,000 tons. We do not want the United States to pay out money for things which our people can produce at home. I may safely say before this association of chemists that sugar is composed of wind and water. Four years ago we produced a fourth of the rice that was consumed in the United States. This year all the rice needed in America, except some special brands, will be produced in this country, and so it goes all along the line. We are endeavoring to grow the things for which we are paying heavily to foreign countries. I do not think it is necessary for us to leave their production to other lands. We have every degree of climate and widely varying conditions from Alaska on the north to the Philippines on the south, and we can produce everything we want. It is the purpose of the Secretary of Agriculture that we shall progress along these lines until whatever we need can be produced somewhere in the United States. In all of these investigations we shall need chemists, and we are going to need them very much.

We have been selling $30,000,000 worth of home-grown tobacco and buying $6,000,000 worth of fine Sumatra tobacco. We have investigated and experimented until now we are able to help the people of New England to produce this fine tobacco. It will only be a question of time when we shall keep that 6 millions of dollars at home. We have determined to produce filler tobacco. We have been trying to find out the climate best adapted to its culture and now we have found two places in the United States where we can grow the finest tobacco under the sun. We find other places where it is only a little too strong; there we shall institute scientific research and grow the tobacco under all possible variations of conditions in order to get just what we want, and while we are doing this we want chemists to watch the plant's progress from the time it takes root. It is wonderful what the American chemist can find out. This work with tobacco means the annual saving of about 14 millions of dollars that we are now paying out for foreign-grown tobacco. We can

eventually produce all this much better at home and supply the world. The prosperity of the United States will be the result of the labors of the American people.

I am obliged to you for sending the committee to wait on me. I hope your stay here will be pleasant and that you will arrive home safely. I bid you good day.

The PRESIDENT. Is it your pleasure that we continue with our program, or shall we adjourn?

Mr. PENNY. I would like to ask the referee on soils if he found any of the surface soils that were not acid?

Mr. HOPKINS. No, sir.

Mr. PENNY. How did you determine that they were acid?

Mr. HOPKINS. By the method I have just described for determining the acidity of soils, and also by making a determination of the carbonates or carbon dioxid.

Mr. PENNY. Did you make the acidity test upon the whole soil, or only on part of it?

Mr. HOPKINS. Ordinarily, we separate material coarser than 1 mm and make our determination upon the fine earth.

Mr. FRAPS. If there is no objection, I would like to present this paper; it will take only about ten minutes.

STUDIES IN NITRIFICATION.

By G. S. FRAPS.

At the last two meetings of this association articles on nitrification have been presented by W. A. Withers and the author. The chief fact brought out in these articles was that in three weeks some soils nitrify ammonium sulphate to a greater extent than cotton-seed meal does, while with other soils the reverse is the case. The explanation for this circumstance advanced in the articles referred to is that the difference is due to the combined influence of three factors:

1. Ammonium sulphate may hinder the action of the nitrifying organisms.
2. The acids produced by their life activity are detrimental to them unless neutralized.
3. There are organisms which convert organic matter directly to nitrites, as well as those which oxidize ammonium salts to nitrites.

It was to test this last hypothesis that the work I am about to describe was instituted. The results obtained at first were so astonishingly irregular that the success of the investigation seemed to be threatened. A search for the cause of the irregularities led, however, not only to some very interesting results in regard to the life history of the organisms, but paved the way for a study of the nature of the nitrifying organisms and laid the foundations for a rational method for studying the nitrifying powers of soils.

METHOD OF WORK.

Two kinds of nitrification tests were made. In one kind the nitrification was carried out in the soil as it came from the field; in the other the tests were carried out in a sterile soil inoculated with an active soil. The first will be called direct nitrification tests; the second, inoculation tests. A large number of both kinds of tests were made in the course of this investigation. The methods used varied slightly at first, but finally the following were adopted as the standard methods:

1. DIRECT NITRIFICATION TESTS.

The sample of soil, as received, was sifted through a 5-mm sieve and mixed thoroughly. Water was determined in it by the usual method, and also its water saturation capacity, as follows:

Fifty grams of the soil were placed in a carbon filter on a perforated porcelain

plate, and the whole weighed. Water was added in quantity a little more than was necessary to saturate the soil, so that a few drops came through, and the tube was allowed to drain, a cork being placed in the mouth of the tube to prevent evaporation from the surface of the soil. After two hours the stem of the tube was dried, and the whole weighed. Allowance was made for the water already in the soil.

In all the nitrification tests 500 grams of soil were used and the quantity of cotton-seed meal, or ammonium sulphate, which contained 0.3 gram nitrogen, together with 2.14 grams calcium carbonate, which is a sufficient quantity to neutralize all the nitric acid and sulphuric acid which would be formed if the ammonium sulphate were completely nitrified. The soil was placed in a porcelain evaporating dish and mixed intimately with the cotton-seed meal (4.30 grams) and calcium carbonate. Sufficient water was then added to bring the water content of the soil to one-third of its saturation capacity, and the whole thoroughly mixed. The mixture was transferred to a pint precipitation jar, or fruit jar, weighed, placed in a water bath in a dark closet, and kept as nearly as possible at 35° C. Every Monday and Thursday the jars were weighed again, and the loss of water replaced in each one. At the end of the period of three weeks the contents of each jar were mixed thoroughly and 100 grams weighed out, extracted with water, and the nitrates determined by the Tiemann-Schulze method. The remainder of the soil was returned to the jar and allowed to nitrify. Nitrates were determined at other periods, as a rule.

In case ammonium sulphate was used for the nitrification the calcium carbonate was mixed with the soil, and water added if necessary. Twenty cubic centimeters of a solution of ammonium sulphate, containing 1.42 grams of the salt, were then added, and the soil was thoroughly mixed. In every case the total amount of water present was kept at one-third of the water saturation capacity of the soil.

It must be noted that the 100 grams of soil taken for analysis did not represent one-fifth of the soil, since the total weight of the soil was 500 grams plus the weight of calcium carbonate, water, and nitrogenous substances. Correction has been made for this fact wherever necessary, but in comparing nitrification in different samples of the same soil no correction has been made, since the same quantity of material was present in each case.

INOCULATION EXPERIMENTS.

For the inoculation experiments a sandy clay soil was used, which had been in the laboratory for three years in the dry condition. It was further sterilized by treatment with chloroform, followed by a drying in an air bath. Its water saturation capacity was 34.3 per cent; so 11.4 per cent water was maintained in it during the tests.

Twenty grams of the soil used for inoculation was mixed with calcium carbonate, and with cotton-seed meal, if it was to be used, in a porcelain dish. The mixture was added to 500 grams of the sterilized soil, mixed thoroughly, a sufficient quantity of water added to bring the water content of the soil to one-third of its water saturation capacity, and the mixture stirred until it appeared uniform. It was then placed in jars, and the experiment conducted as described above.

When ammonium sulphate was used, the soil used for inoculation was mixed with calcium carbonate, and then with the soil. Water was then added, and finally 20 cc of the solution of ammonium sulphate already referred to. It was considered possible that the strong solution of ammonium sulphate might destroy some of the nitrifying germs if it came in contact with them before it was diluted.

In most of the experiments described in this article, the tests were carried out in duplicate. In many cases the agreement between the duplicates was satisfactory, but at times a jar would deviate from the normal. In such cases due judgment must be used in selecting the results. It can not be expected, in dealing with microscopic organisms, which are liable to vary in their activity, and sometimes for no known reason, that the same agreement can be obtained as in ordinary chemical analysis.

Description of Soils.

1746. Sandy clay soil from a wheat field on college farm; little humus; saturation capacity, 33 per cent.

1746a. A second sample, taken two months later.

1747. Sandy clay soil, sterilized as described previously; used in all inoculation experiments.

1748. Dark loam soil from a peach orchard on the experiment station farm; contains humus; saturation capacity 34 per cent.

1764. Black sandy soil from the Florida experiment station; contained only 0.5 per cent of water when it arrived, and had little nitrifying power.

1764a. A second sample, which had been kept in a well-closed fruit jar since the summer of 1901, and was still quite moist.

1766. Loam from a flower bed on college lawn; contains much humus.

1766a. A second sample, taken three weeks later.

1768. A garden soil.

1772. Sandy soil from the test farm of the North Carolina department of agriculture at Tarboro, N. C.; contained only 1.85 per cent water when received, but appeared moist; saturation capacity, 27.3 per cent.

1779. Poor, light, sandy soil from college farm; no humus; saturation capacity, 27 per cent.

1780. Rich, dark, sandy soil from college farm; contains much humus; saturation capacity, 46 per cent.

1781. Black, sandy soil from garden of State Chemist B. W. Kilgore, at Raleigh, N. C.; contains much humus; saturation capacity 42.5 per cent.

Acknowledgment is hereby made to Chemist H. K. Miller, of Florida, and State Chemist B. W. Kilgore, of North Carolina, for their kindness in furnishing samples of soil.

Variations in the Nitrifying Powers of Soils.

The irregularities referred to in an earlier part of this paper consisted in variations in the nitrifying power of the same soil. Samples taken at one time would nitrify vigorously, while another sample, taken a little later, would hardly nitrify at all, under the same conditions. For example, a soil taken from a wheat field May 28 nitrified 143 mg of nitrogen per kilo of soil in three weeks, while a sample of the same soil taken from the same place three weeks later nitrified only 20 mg in the same time.

Similar irregularities were observed in inoculation tests with soils. These variations are due to variations in the number and in the activity of the germs contained in the soil. The causes of the variations appear to be as follows:

1. *Variations in the water content of the soil.*—It is a well known fact that a decrease of the moisture of a soil below a certain limit is prejudicial to the activity of the nitrifying organisms. If the soil dries out, the organisms die, or become inactive; if it is moist, they thrive and increase.

2. *Variations in temperature.*—Prolonged cold decreases the numbers of the nitrifying organisms, while warmth is beneficial, and causes them to multiply.

3. *Abundance of food.*—The number of nitrifying organisms in different soils would vary somewhat with the food supply for them in the soil.

4. *Periodicity of the organisms.*—When the progress of nitrification is studied in soils under uniform conditions of moisture and temperature and plant food, it is seen that there are periods of activity of nitrification, preceded and followed by periods of comparative rest, during which much smaller quantities of nitrates are produced. This periodicity will now be discussed.

Periodicity of Nitrification.

In a number of experiments conducted during the course of this investigation, the rate of nitrification was studied by making determinations of nitrates in the soils at

the end of three weeks, and at the ends of succeeding weeks. The quantity of nitrogen oxidized per week during each period shows the rate of nitrification in the soil. It is easily seen from a study of the results that the activity of the organism is periodical, and that a period of activity is preceded and followed by a period of comparative inactivity. The periodicity of the rate of nitrification of ammonium sulphate and cotton-seed meal is shown very strikingly in the four curves in figure 3. The periods are plotted as abscissae, and the number of milligrams of nitrogen oxidized

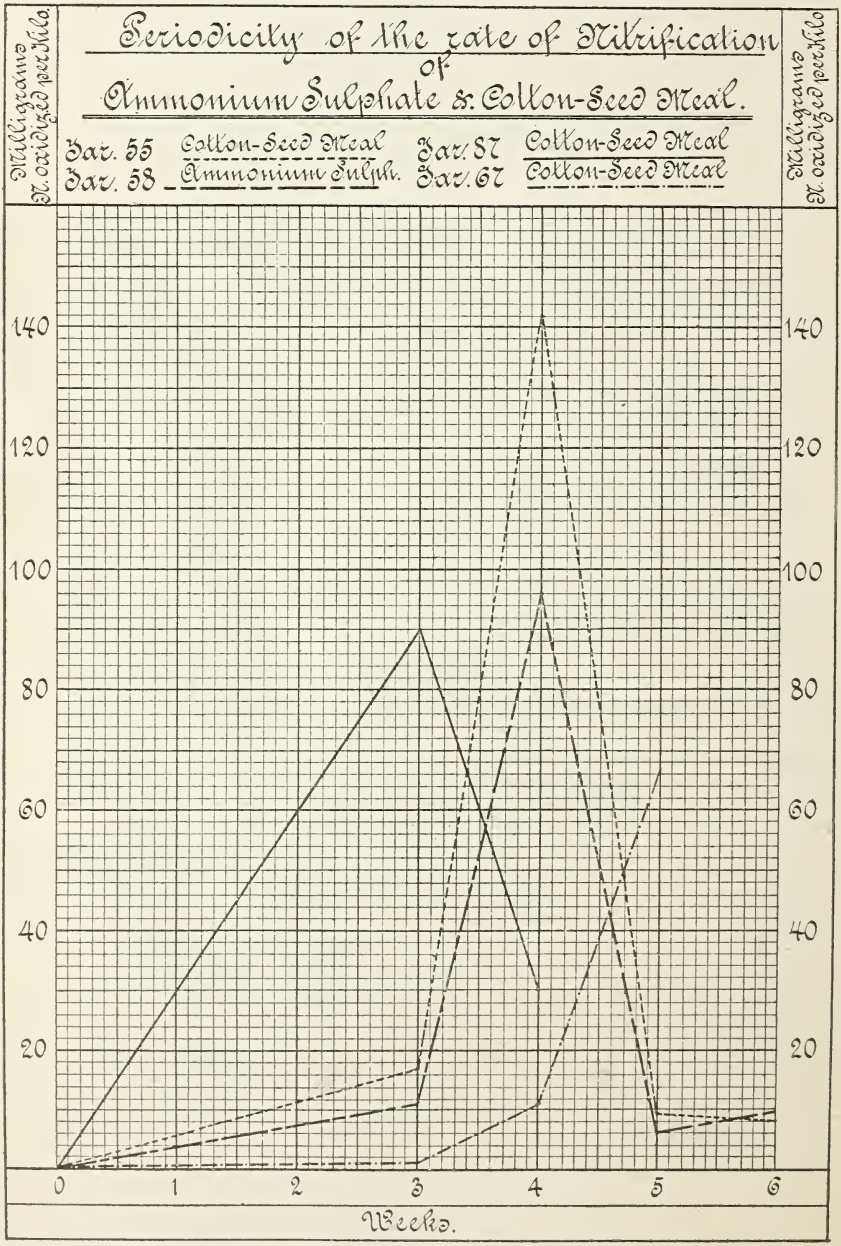

FIG. 3.—Periodicity of the rate of nitrification of ammonium sulphate and cotton-seed meal.

per kilo of soil per week during each period as ordinates. The curves were chosen to show how the period of greatest activity of nitrification may come during the first three weeks, or during the fourth week, or the fifth week, according to the condition of the soil at the time of starting the experiment.

Table I exhibits the rate of nitrification in 21 jars of soil, conducted in nine sets, and with organisms derived from seven different soils.

TABLE I.—*Rate of nitrification.*

[Nitrogen per kilo of soil oxidized per week.]

Soil and nutrient.	First three weeks.	Fourth week.	Fifth week.	Sixth week.	Total.
	Mgs.	*Mgs.*	*Mgs.*	*Mgs.*	*Mgs.*
Soil 1748, inoculation tests:					
Jar 55, cotton-seed meal	17	141	9	8	210
Jar 56, ammonium sulphate	5	59	.....	[a]37	138
Jar 57, cotton-seed meal	12	109	[b]—57	5	91
Jar 58, ammonium sulphate	11	96	6	9	143
Soil 1764, inoculation tests:					
Jar 67, cotton-seed meal	2	94	34	.....	133
Jar 68, ammonium sulphate	2	53	8	.....	69
Soil 1766, inoculation tests:					
Jar 72, cotton-seed meal	10	106	0	.....	135
Jar 74, ammonium sulphate	2	61	[b]—9	.....	57
Soil 1772, direct nitrification:					
Jar 77, cotton-seed meal	2	63	.....	.....	70
Jar 79, ammonium sulphate	1	1	0	.....	4
Soil 1772, inoculation tests:					
Jar 81, cotton-seed meal	7	108	.....	.....	130
Jar 83, ammonium sulphate	3	62	.....	.....	70
Soil 1781, inoculation tests:					
Jar 91, cotton-seed meal	31	66	.....	.....	159
Jar 93, ammonium sulphate	25	49	.....	.....	124
Soil 1781, direct nitrification:					
Jar 85	7	5	.....	.....	26
Jar 87, cotton-seed meal	90	30	.....	.....	300
Jar 90, ammonium sulphate	93	39	.....	.....	319
Soil 1746, direct nitrification:					
Jar 47, cotton-seed meal	12	.....	[c]69	42	218
Jar 49, ammonium sulphate	7	.....	[c]28	52	129
Soil 1768, inoculation tests:					
Jar 62, cotton-seed meal	1	13	67	.....	83
Jar 65, ammonium sulphate	2	9	64	.....	79

[a] Mean of fifth and sixth week. [b] Denitrification took place. [c] Mean of fourth and fifth weeks.

An examination of the table brings out the following facts:

1. The rate of nitrification reaches a maximum, and then decreases.

2. The decrease in the rate of nitrification is not due to lack of nitrogen to nitrify. The soil contains 532 mg of nitrifiable nitrogen per kilo. The total amount of nitrogen oxidized in each jar is given in the table, and is less than half of the amount present in the soil in most cases.

3. The period of greatest energy of nitrification has come, as a rule, in the fourth week. This is the case with six of the nine sets of soils given in Table I. In one set it came in the fifth week, in one set during the first three weeks, and in one during either the fourth or fifth week.

4. The period of greatest energy of nitrification comes at the same time, under the same conditions, whether the nitrogen to be oxidized is supplied by ammonium sulphate or by cotton-seed meal.

5. The quantity of nitrogen oxidized during the first three weeks of a nitrification experiment depends on the activity of the organisms in the soil taken for the experiment, as well as on the number of germs present. In the same soil, and under the same conditions, it may happen that a sample taken at one time will oxidize a large quantity of nitrogen during the first three weeks, while a later sample will not nitrify to any great extent during that time, but will do so if kept a little longer.

CAUSE OF PERIODICITY.

The explanation of the variable rate with which nitrification takes place from time to time is to be found in the life history of the nitrifying organisms. There seems to be a period of multiplication of the germs, during which little nitrification takes place, then a period of multiplication and nitrification, followed by a period of multiplication without nitrification again. The reasons for this last statement will be developed later. After a time the number of nitrifying organisms no longer increases, but diminishes, on account of the consumption of nitrifiable matters. How long a period of time it takes for a group of the nitrifying organisms to complete this cycle of changes can not be stated. The maximum period of time required in any of the experiments here given for the maximum of activity of nitrification to occur was five weeks.

The life history of the nitrifying bacterium has a parallel in that of the bacteria which assimilate nitrogen on the roots of legumes. Cultivated outside of the plant, it has not yet been found possible to cause them to assimilate more than 7 mg per gram of sugar consumed by them, a very small quantity. When growing in nodules on leguminosæ, according to Nobbe and Hiltner, the bacteria are in the nature of parasites until they are transformed into bacteriod forms, and then the plant begins to receive the benefit of nitrogen assimilated from them. There thus appears to be two stages in the life of this organism, first a period of multiplication with little assimilation of free nitrogen, then a period in which the form of the bacteria changes, and assimilation of nitrogen takes place. As was stated, this life history is parallel to that of the nitrifying organisms.

Inoculation Energy of Soils.

By the inoculation energy of a soil, we mean its power to induce nitrification in a sterile soil provided with nitrogenous substances and kept under favorable conditions. For the measure of the inoculation energy of a soil there has been taken the quantity of nitrates formed in three weeks in the sterile soil used throughout these experiments, inoculated with the soil to be tested. The method of conducting inoculation tests has already been described. The inoculation energy of a soil depends upon the number of germs in the soil and on their activity. Any influence which decreases the number of germs in a soil diminishes its inoculation energy.

The inoculation energy of certain soils or cultures was studied in two ways. The first experiments consisted in a comparison of the inoculation energy of the soil with the quantity of nitrates formed in it during the three weeks previous to starting the inoculation test, and were as follows: The soils in Series I were allowed to nitrify three weeks and the quantity of nitrates in them determined. Series II was then prepared by inoculation from Series I. At the end of a second three weeks Series II was analyzed and inoculations prepared from it, forming Series III. It should be stated that the soils in Series I were all inoculation tests, so that the soils used throughout the experiments are exactly the same, and the results are directly comparable. The results are given in Table II.

TABLE II.—*Inoculation energy of soils.*

[Nitrogen oxidized per kilo of soil.]

Nutrient.	Series I.	Series II.[a]	Series III.[a]	Ratio I: II.	Ratio II: III.
	Mgs.	*Mgs.*	*Mgs.*	*Mgs.*	*Mgs.*
Cotton-seed meal	182	52	81	3.5:1	0.6:1
Ammonium sulphate	176	15	4	12:1	3.8:1
Cotton-seed meal	73	35	12	2.1:1	2.9:1
Ammonium sulphate	67	32	25	2.1:1	1.3:1

[a] Series II represents the inoculation energy of Series I at the end of three weeks; Series III the inoculation energy of Series II.

The ratio of Series I to Series II, and of Series II to Series III, shows the effect of dilution of the actively nitrifying soil with 25 times its weight of sterile soil, and providing a quantity of nitrogenous matter. The series was not carried out in duplicate, and some of the variations are probably due to a jar going wrong. Excluding the greatest variations, the ratio of the quantity of nitrogen oxidized in the first three weeks to the quantity oxidized in the soil inoculated from it in the succeeding three weeks varies from about 2:1 to 3:1. As will soon be seen, however, this ratio depends on the activity of the inoculating soil or on the number of organisms present in it.

The second method of studying the inoculation energy of soils consisted in determining the inoculation energy of several soils at different periods during nitrification in order to see what change it undergoes. Four jars of soil were studied for the main experiment. They were kept under standard conditions and nitrates determined in samples taken at the end of three, four, five, and six weeks, respectively. At the end of three weeks Series II was prepared by inoculation from Series I. At the end of four weeks Series III was prepared from Series I, and Series IV was prepared at the end of the fifth week. The quantity of nitrogen in the form of nitrates in the soils of Series II, III, and IV at the end of three weeks represents, therefore, the inoculation energy of the soils of Series I at the end of different periods of time. The unbroken curves in figures 4 and 5 show the change in the inoculation energy of the four samples of soils with time. The inoculation energy of the soils increases regularly with the time during which nitrification takes place. It might be imagined that the inoculation intensity of a soil would vary somewhat as its energy of nitrification, but this is not the case, as may be seen by comparing figures 3 and 4. During the fifth week the nitrification intensity of the soil is very much lower than during the fourth week, while its inoculation intensity is higher than before.

There seems to be a very close relation between the inoculation intensity of a soil and the total quantity of nitrogen oxidized in it, as can be seen by comparing the unbroken curves in fig. 4 with the broken curves, which represent the total quantity of nitrogen oxidized. Even in the case in which denitrification took place (jar 57) the inoculation intensity of the soil exhibits a decrease corresponding with the decrease in the total quantity of nitrates in the soil. Table III contains the figures which were obtained in the inoculation experiment, and also gives the results of an experiment on soil No. 1781, which leads to the same conclusion as the other one. It gives the inoculation energy of the soils at the end of each period, and also the total quantity of nitrates present in them.

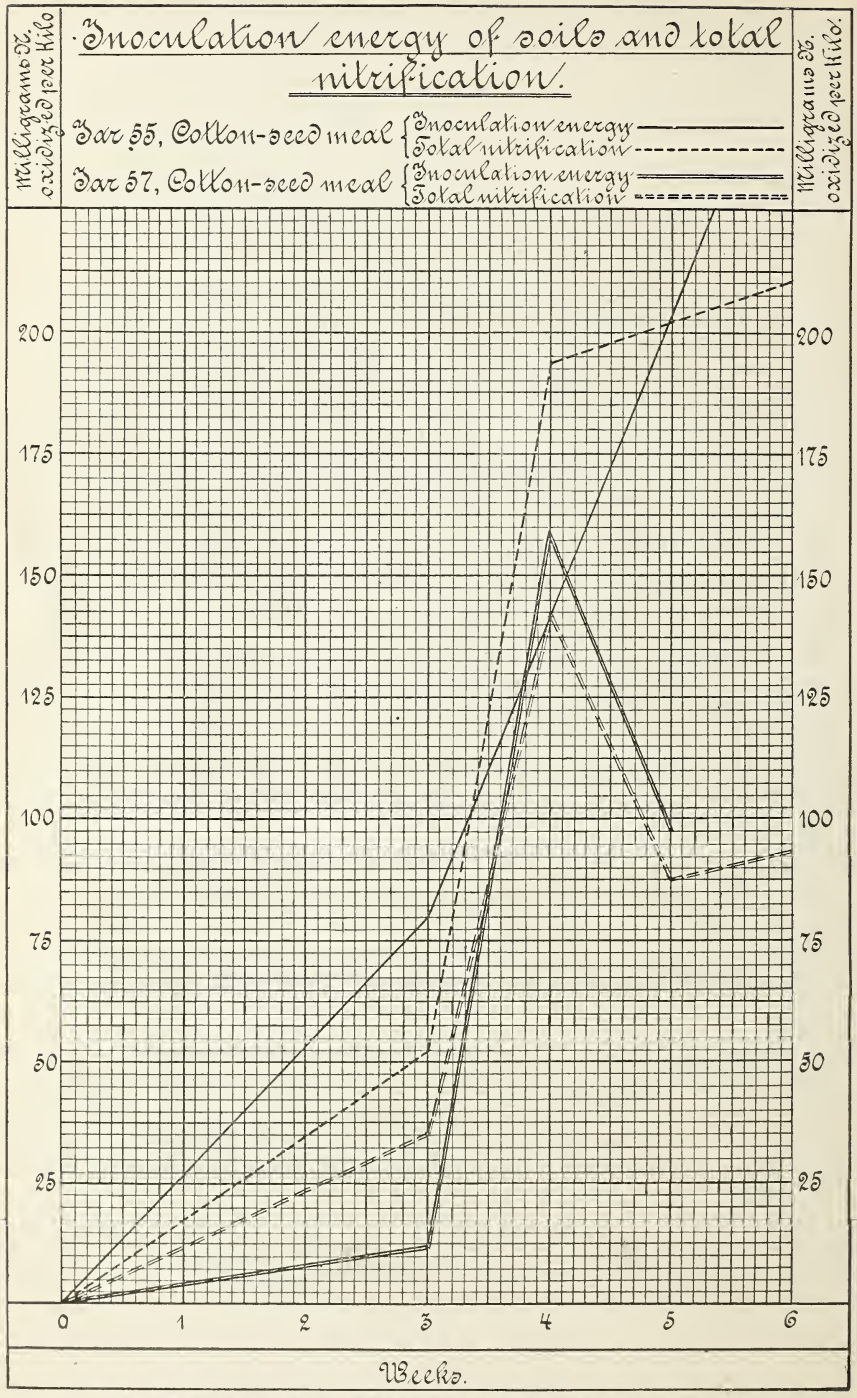

FIG. 1.—Inoculation energy of soils and total nitrification (cotton-seed meal).

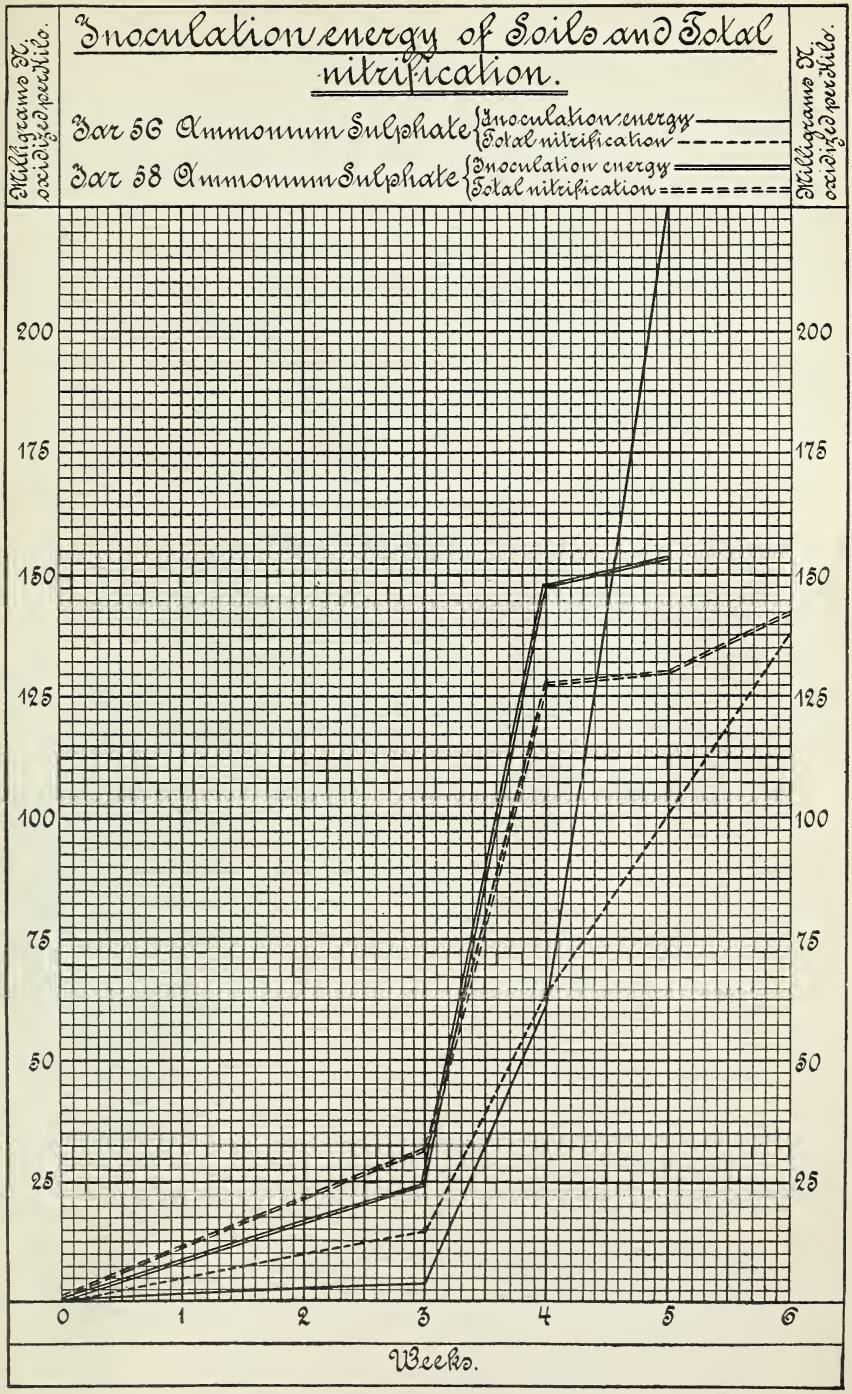

FIG. 5.—Inoculation energy of soils and total nitrification (ammonium sulphate).

TABLE III.—*Effect of time on inoculation energy.*

[Nitrogen oxidized per kilo of soil.]

Nutrient.	Three weeks.		Four weeks.		Five weeks.		Six weeks—total nitrification.
	Total nitrification.	Inoculation energy.	Total nitrification.	Inoculation energy.	Total nitrification.	Inoculation energy.	
Series A, derived from soil No. 1748:	*Mgs.*	*Mgs.*	*Mgs.*	*Mgs.*	*Mgs.*	*Mgs.*	*Mgs.*
Jar 55, cotton-seed meal	52	81	193	141	202	205	210
Jar 56, ammonium sulphate	15	4	63	57	.....	219	138
Jar 57, cotton-seed meal	35	12	144	158	86	97	91
Jar 58, ammonium sulphate	32	25	128	147	133	153	.....
Series B, derived from soil No. 1781:							
Jar 91, cotton-seed meal	93	115	159	123	.....	.....	.....
Jar 92, cotton-seed meal	113	99	171	131	.....	.....	.....
Jar 93, ammonium sulphate	75	60	124	75	.....	.....	.....
Jar 94, ammonium sulphate	24	75	138	139	.....	.....	.....

An examination of the table leads to the following conclusion:

1. The inoculation energy of a soil provided with nitrifiable matter, and kept under favorable conditions, increases with time.

2. The inoculation energy of the soil has a close relation to the total quantity of nitrogen oxidized in the soil.

3. The ratio of the total quantity of nitrogen oxidized in the soil to its inoculation energy decreases from 3:1 or 2:1 in three weeks, to 1:1 in longer periods.

4. This ratio depends to some extent on the inoculation energy of the soil.

CAUSE OF VARIATIONS IN INOCULATION ENERGY.

The changes in the inoculation energy of a soil, as described above, are probably due to the following causes:

1. *Increase in the number of germs present in the soil.*—In a soil provided with an abundance of food for the nitrifying organisms, and kept under favorable conditions, it is self-evident that the number of the bacteria will increase, for a time at least. This increase seems to continue during the whole period of time taken in the study of the changes in the inoculation energy of the soils. In time, the number of bacteria must remain stationary, and then begin to decrease as the food supply diminishes.

2. *Increase in the activity of the organisms.*—At the same time that the number of nitrifying organisms increases, there seems to be an increase in their activity. They either multiply more rapidly, or grow in power to nitrify. There may be some connection between this change and the periodicity which we have observed in the rate of nitrification of ammonium sulphate and cotton-seed meal. It is also analogous to the increase in activity or "virulence" of nitrogen-assimilating bacteria under cultivation.

NATURE OF THE NITRIFYING ORGANISMS.

In previous articles from this station, already referred to, it has been shown that some soils nitrify cotton-seed meal to a greater extent than ammonium sulphate in three weeks, while with other soils ammonium sulphate is oxidized more rapidly. The explanations advanced for this fact have already been given. The experiments now to be described were designed to test the third hypothesis, namely, that there

are organisms which convert organic matter directly to nitrites, as well as those which oxidize ammonium salts to nitrites.

In the first place, Is the difference in the rate of nitrification of cotton-seed meal and ammonium sulphate due to the nature of the soil, or to the nature of the organisms in it? The answer to this question is, that the difference is due most largely to the germs, though the nature of the soil is not without its influence.

The experiments which lead to this answer are based on the following considerations: If different samples of a sterile soil are inoculated with the germs from a variety of soils, and allowed to nitrify ammonium sulphate and cotton-seed meal under exactly the same conditions, there will be no difference in the relative amounts of cotton-seed meal and ammonium sulphate nitrified, unless the organisms derived from the different soils are different. That is to say, the soil and other conditions of the experiment do not vary, with the exception of the germs, which do vary.

Table IV contains the results of these experiments. The table shows the number of milligrams of nitrogen in the form of ammonium sulphate, and in the form of cotton-seed meal, oxidized in three weeks in the same sterilized soil inoculated with a number of soils.

TABLE IV.—*Relative amounts of cotton-seed meal and ammonium sulphate nitrified by inoculation of a soil.*

[Nitrogen oxidized per kilo of soil.]

Soil used for inoculation.	Cotton-seed meal.	Ammonium sulphate.	Ratio.
	Mgs.	*Mgs.*	
Loam soil, 1748	73	66	1:0.9
Sandy clay soil, 1746a	100	53	1:0.5
Black sandy soil, 1764a	99	61	1:0.6
Loam soil, 1776a	29	7	1:0.3
Sandy soil, 1772	23	10	1:0.4
Black sandy soil, 1781	100	84	1:0.8

The relative amounts of cotton-seed meal and ammonium sulphate nitrified varies from 1:0.3 to 1:0.9, according to the soil used for the inoculation. This variation is certainly evidence that the variation in the comparative rate of nitrification of ammonium sulphate and cotton-seed meal is due to variations in the organisms in different soils. That is to say, it seems that there are two classes of nitrifying bacteria.

When the nitrification in the inoculated soils is allowed to continue for a longer period of time than three weeks, the relative amount of nitrogen oxidized sometimes varies. Table V exhibits the variation in the relative amounts of nitrogen oxidized in varying times in ammonium sulphate and cotton-seed meal. The sterile soil presents conditions favorable to the development of both classes of organisms, and we might expect both to develop vigorously, but this does not prove that there is no difference in the organisms which effect nitrification in different soils. Even if we exclude the cases of variation, there is sufficient evidence to establish the point that there is a difference.

TABLE V.—*Effect of time on nitrification of cotton-seed meal and ammonium sulphate in inoculated soil.*

[Nitrogen oxidized per kilo of soil.]

Soil No.	Time.	Cotton-seed meal.	Ammonium sulphate.	Ratio.
	Weeks.	*Mgs.*	*Mgs.*	
1746a ..	Five	100	53	1:0.5
	Six	104	156	1:1.5
	Seven	129	187	1:1.5
1768....	Three	3	7	[a]1:2.3
	Four	16	15	1:1
	Five	80	79	1:1
1764....	Four	99	61	1:0.6
	Five	133	74	1:0.6
1766a ..	Three	29	7	1:0.3
	Four	134	68	1:0.5
	Five	435	76	1:0.6
1772....	Three	23	10	1:0.4
	Four	130	70	1:0.5
1781....	Three	100	84	1:0.8
	Four	165	131	1:0.8

[a] Excluded on account of the small amount of nitrification during this period.

Another evidence in favor of the view that there are variations in the nitrifying organisms in soils is offered by a comparison of the relative amounts of cotton-seed meal and ammonium sulphate nitrified in the soil itself, and in the soil inoculated from it. The figures are given in Table VI. It is seen at a glance that, though the ratio of nitrification of ammonium sulphate and cotton-seed meal varies from soil to soil, there is comparatively little variation from a soil to its inoculation This is a further evidence that the variations are due to the germs in the soils.

TABLE VI.—*Relative amounts of cotton-seed meal and ammonium sulphate nitrified in soils and in inoculations from them.*

[Nitrogen oxidized per kilo of soil.]

Soil No.	Method.	Cotton-seed meal.	Ammonium sulphate.	Ratio.
		Mgs.	*Mgs.*	
1748....	Direct	212	176	1:0.8
	Inoculation	73	66	1:0.9
1746....	Direct	176	77	1:0.45
	Inoculation	100	53	1:0.53
1772....	Direct	5	3	1:0.6
	Inoculation	23	12	1:0.5
1781....	Direct	284	267	1:0.9
	Inoculation	105	85	1:0.9

If there are two classes of nitrifying organisms in the soil, it should be possible to increase the relative numbers of one class by the cultivation of it in a soil containing cotton-seed meal, and the relative numbers of the other class by cultivation in a soil containing ammonium sulphate.

If soils containing cotton-seed meal and ammonium sulphate are inoculated from these cultures, the relative amounts of cotton-seed meal and ammonium sulphate nitrified should be different in the two cultures, though they are both derived originally from the same soil. This experiment has been tried and has succeeded, and

the results of the work are given in Table VII. In each case the cultures made in cotton-seed meal nitrified a proportionally larger quantity of cotton-seed meal than the cultures made with ammonium sulphate. Also, the cultures made with ammonium sulphate nitrified a larger proportion of the nitrogen in the form of ammonium sulphate than in the form of cotton-seed meal. It is thus possible to increase the relative numbers of the one group of organisms by cultivating them in a soil provided with the appropriate food.

TABLE VII.—*Effect of cultivating the organism on the relative amounts of cotton-seed meal and ammonium sulphate nitrified.*

[Nitrogen oxidized per kilo of soil.]

Conditions.	Cotton-seed meal.	Ammonium sulphate.	Ratio.
Set I (1746):	*Mg.*	*Mg.*	
Direct, 5 weeks	176	76	1:0.5
Inoculation, 5 weeks	135	194	1:1.4
Grown in cotton-seed meal	225	157	.....
	240	167	.....
Mean	233	162	1:0.7
Grown in ammonium sulphate	190	200	.....
	189	.....	.....
Mean	190	200	1:1.05
Set II (1772):			
Direct	5	3	1:0.6
Inoculation	256	70	1:0.4
Grown in cotton-seed meal	158	34	.....
	130	47	.....
Mean	143	41	1:0.3
Grown in ammonium sulphate	118	70	.....
	114	57	.....
Mean	116	64	1:0.6

An attempt might be made to explain the preceding statements on the theory that two groups of organisms take part in the process of nitrification in soils, one group which nitrifies ammonium salts, and one which prepares organic matter for the first group by converting it into ammonium salts. Undoubtedly both classes of organisms of this kind do exist in soils. When the organisms are cultivated in a soil containing ammonium sulphate, the germs which prepare cotton-seed meal for nitrification increase only at the expense of the organic matter in the soil, and so the soil loses in power to nitrify cotton-seed meal and gains in power to nitrify ammonium sulphate. When the organisms are cultivated in a medium containing cotton-seed meal, the organisms which prepare organic matter for nitrification increase, and so the soil gains in power to nitrify cotton-seed meal. But just here the theory fails to explain all the facts. Any increase in the power of a soil to nitrify cotton-seed meal must, according to this theory, be conditioned on an increase in the power or number of the germs which oxidize ammonium salts, since the cotton-seed meal is first converted into ammonium salts. But our experiments show that an increase in the power to nitrify cotton-seed meal is accompanied with a decrease in power to nitrify ammonium sulphate. This fact can not be reconciled with the above theory, but is in favor of the view that soils contain organisms which nitrify organic matter directly. It is very evident that the process of nitrification is a very complex phenomenon, participated in by a number of classes of bacteria.

Determination of the Nitrifying Power of Soils.

The work recorded in this paper serves as the basis for a method of determining the relative nitrifying power of two or more soils. In order to compare the nitrifying power of two soils, it is necessary that they should be placed under favorable conditions for nitrification, the conditions being exactly alike for both soils. Each soil should contain the same number of organisms of nitrification, with the same degree of activity, and the temperature, water content of the soil, and other conditions should be the same.

The nitrifying power of two soils may be compared in two ways. Of these the second is to be preferred, since it gives more exact results:

Method I.—By comparison of direct nitrification and inoculation tests. Nitrification experiments and inoculation tests are made on the soil as it comes from the field by methods described in the earlier part of this paper. The sterilized soil used for the inoculation tests should be of good quality. If the soil is of good quality, the quantity of ammonium sulphate and cotton-seed meal nitrified in it directly in three weeks should be two to three times the quantity nitrified in the inoculation tests, but if the soil is of poor quality, nitrification will go on more rapidly in the inoculated soil than in the soil itself, although the inoculated soil starts with only one twenty-fifth as many nitrifying germs. The application of the method is illustrated in Table VIII. In two of the soils the ratio of the nitrogen oxidized in the soil and in the inoculation from it is between 2:1 and 3:1, while in the soils which are not such favorable mediums for nitrification the ratio is between 0.4:1 and 0.1:1. In the case of soil No. 1772 a continuation of the experiment for a fourth week shows that it is a much more favorable medium for the nitrification of cotton-seed meal than ammonium sulphate. As stated, the second method now to be described is to be preferred for the determination of the nitrifying power of soils.

Table VIII.—*Relative amounts of nitrogen oxidized in soils and in inoculations.*

Conditions.	Direct.	Inoculation.	Ratio.
GOOD SOILS.			
1748, loam soil, with humus:	*Mg per kilo.*	*Mg per kilo.*	
Cotton-seed meal	182	73	2.5:1
Ammonium sulphate	176	67	2.7:1
1781, garden soil, rich in humus:			
Cotton-seed meal	270	93	2.9:1
Do	299	113	2.6:1
Ammonium sulphate	256	75	3.4:1
Do	281	94	3.0:1
POOR SOILS.			
1741, loam soil, little humus:			
Cotton-seed meal	37	102	0.3:1
Ammonium sulphate	20	53	0.4:1
1772, sandy soil:			
Cotton-seed meal	7	21	0.3:1
Do	2	24	0.1:1
Ammonium sulphate	3	8	0.3:1
Do	3	12	0.2:1
1792, 4 weeks;			
Cotton-seed meal	70	156	0.4:1
Do	61	130	0.5:1
Ammonium sulphate	4	70	0.06:1
Do	3	.....	.....

Method II.—In this method the soils to be tested are compared in their nitrifying power with some standard soil, of good quality, a large supply of which has been secured. All of the soils are sterilized by heating at a moderate temperature for some time, treated with chloroform, and heated again to drive off the chloroform. The heat used in drying the soil should not be too high. Determinations of the water saturation capacity of the soils are made. Inoculation tests are then instituted on the soils as described in the earlier part of the paper. All the soils to be compared should be inoculated at the same time and with the same soil, so that each jar of soil will contain exactly the same number of nitrifying organisms with the same inoculation energy. As the number and inoculation energy of nitrifying organisms in a soil are subject to variations from day to day, it would not do to inoculate some of the soils one day and the remainder the next, but with every set of soils a comparison should be made with the standard soil.

At the end of three weeks a determination of nitrates is made in every sample of soil, and since all conditions are the same, with the exception of the soils, the results are directly comparable, and represent the nitrifying power of the soils. If the soil used for the inoculation has a low inoculation intensity, the time of the experiment should be extended. Table IX shows the application of this method to the determination of the relative nitrifying power of three soils.

TABLE IX.—*Relative nitrifying powers of soils.*

[Nitrogen oxidized per kilo of soil.]

Nutrient.	Poor sandy soil, No. 1779.	Rich sandy soil, No. 1780.	Soil, No. 1747.	Ratio.
	Mgs.	*Mgs.*		
Cotton-seed meal	2	116		
Do	2			
Mean	2	116		1:56
Ammonium sulphate	3	68	71	
Do	3	77	84	
Mean	3	73	77	1:24:26

With these soils the quantity of water used was one-third of their saturation capacity, which of course varies for the different soils. Whether this quantity of water should always be used or not, must be decided by subsequent experiments.

Referring to the table, it is seen that the poor sandy soil has little power of nitrification. The sandy soil used to illustrate Method I has also little power of nitrification, and less for ammonium sulphate than cotton-seed meal. On the other hand, the sandy soil in Table IX, which contains much humus, has a high power of nitrification. These results illustrate the importance of a study of the comparative nitrifying powers of soils.

Mr. EWELL. I would like to ask Mr. Fraps one or two questions. How are the moisture and temperature controlled?

Mr. FRAPS. By weighing the jar containing the soil and replacing the water lost twice a week. The jar was placed in a water bath and kept as nearly as possible at 35° C.

Mr. EWELL. What was the quantity of soil used?

Mr. FRAPS. Five hundred grams. All the details will be found in the paper as published in full.

Mr. VAN SLYKE. I move that we adjourn until 1.30 p. m.

The motion prevailed and the meeting adjourned at 12 o'clock noon.

FRIDAY—AFTERNOON SESSION.

The meeting was called to order by the president at 1.30 p. m.

The PRESIDENT. If there is no objection, we will proceed with the discussion on soils.

Mr. VEITCH. I have been much interested in the question of soil acidity and in the method with which Mr. Hopkins has been working. In the Bureau of Soils we also have been working on methods for the determination of acidity. It seems to me that the first thing we need to do is to define acidity and settle upon an indicator which shall be the standard by which to judge the reaction of soils. Many of the acids that may be present in soils are so weak that they give no certain reaction with most indicators, except in concentrations greater than probably exist in most soil solutions. After a great deal of experimenting with many indicators I have adopted the following method for determining the reaction of a soil:

Ten grams of soil are treated with 100 cc of distilled water in a Jena flask and allowed to stand overnight. Fifty cc of the supernatant liquid are carefully drawn off and boiled with a few drops of phenolphthalein in a covered Jena beaker until the appearance of the pink color or to a volume of about 5 cc with no development of color. The pink color shows the soil to be alkaline, while no color shows it to be acid or neutral.

For the quantitive determination of a soil acidity I use the following method:

To three portions of soil, each consisting of as many grams as the standard limewater contains milligrams of lime (CaO) per cc, add 50 to 60 cc of distilled water and different amounts of standard limewater. For example, to the first add 10 cc, to the second 20 cc, and to the third 30 cc of limewater. Dry down at once on the steam bath, transfer to stoppered Jena flasks with 100 cc of distilled water, allow to stand overnight, with occasional shaking, draw off or filter off 50 cc, place in a Jena beaker, add a few drops of phenolphthalein solution, and boil until the appearance of the pink color, or in case no color is developed, to a volume of about 5 cc. Then with the two portions of treated soils, one of which has been rendered alkaline by the limewater and the other of which is still acid, as guides, prepare three fresh portions of 10 grams each and add limewater as before, except that the amount added to a dish differs from that added to another by only 1 or 2 cc. Dry, take up with 100 cc of water, allow to stand, draw off, and treat exactly as before. The smallest amount of limewater which gives the characteristic pink color is taken as the acidity equivalent of the soil. Each cubic centimeter of standard limewater is equivalent to an acidity of 0.01 per cent expressed as calcium oxid.

The method has been applied to quite a number of soils with very satisfactory results. So far we have had no opportunity to observe the effect on crop production of applications of lime in the amount called for by the method. In quite a number of determinations of the reaction of the soils of clover (red) fields I have never found the acidity of those portions bearing a vigorous crop to exceed 0.0013 gram of calcium oxid per 10 grams of soil, while no clover was found on those

portions of the field having an acidity equal to 0.002 gram or more calcium oxid per 10 grams of soil, though these portions may have been only 1 or 2 feet distant from the first-mentioned portions bearing a good growth. These results lead me to hope that the method has an agricultural significance. Work along this line has been planned for the coming year.

Mr. Wiley. I have been much interested in the papers on soils and in the discussion. Of course we all recognize the fact that the soil is the most important subject of agricultural research, in one sense of the word at least, and that the methods which the physicists and chemists devise for the amelioration of the soils are not only of scientific interest but of immense economic importance. The surface of the earth instead of growing larger is growing smaller; therefore, as the area of the earth can not be increased with the increasing population and demand for food unless we have some method for increasing the productivity of the soil, the time will come when the limit to population will be determined by the supply of food. The great question is how to increase the productivity of the soil. One of the important works of agricultural engineering is found in irrigation, by which we may increase the areas which can be used for agricultural purposes. Therefore, it seems that we must look in part to this source to increase the food supply. It is necessary, first, to increase the productivity of the areas which are already under cultivation, and second, to make those areas available which by reason of insufficient rainfall are not tillable. We know what scientific agriculture has done in the way of conserving plant foods and in supplying additional plant foods to the soil. All of the problems which have been presented in these papers are of enormous importance in these investigations. Little was known in a practical way about soil acidity until the investigations of the Rhode Island station brought out the relative acidity of soils. Twelve years ago we studied in Florida absolutely sterile soils, and in the potted soils of that region the plants would make a vigorous start for a few days, but would never reach maturity. Of course the trouble here was that the acidity of the soil prevented nitrification. The investigations at the Rhode Island station showed how fields which were very sterile could be made productive by correcting the acidity of the land. Now we have these investigations to determine the degree of acidity, which we listened to this morning, so that the farmer may not only be able to tell whether his soil is acid, but how much calcium carbonate or lime may be needed to correct this condition.

The distribution of the crops is largely determined by the character of the soil. The old discussion as to whether you can tell anything about a soil by chemical and physical tests has also been brought before us this morning. The soil when left to itself does determine the character of the native crop. The character of the natural growth

of the forest is largely determined in any given locality by the nature of the soil itself. I was brought up in a locality where we had almost all kinds of forest trees and the growth of the forest depended largely on the condition of the soil. The best way to study the effect which a soil itself produces upon a crop is to go into the forest and see what it does in the natural state and afterwards study it in an artificial condition.

We know that pine trees grow in the sand, where maple and oak trees will not grow, and, when left to natural causes in the struggle for existence, that plant which is best adapted to the soil and the rest of the environment is the one that survives. It is clear to all, I think, that we should study and know the influence of the soil upon the character and growth of the crop which is to be grown upon it. We all know that the soil which is suitable for growing vegetables is not best adapted to wheat growing. More clay is required for wheat. It is either a question of plant food in the soil or the physical state of the soil which determines this. The physical state of the soil is largely influential in determining these natural growths. We know that oak trees grow on stiff flat soil, while maples and poplars grow in the open porous soils. In southern Indiana, years ago, the people would not try to grow wheat on fields from which oak trees were cleared. They thought wheat would not grow where the oak trees grew—in a flat stiff soil—but that it must be grown on rolling limestone land where the maples grew. Early settlers would first go where the maple trees grew, and you will notice that where the oak trees grew was the last place to be settled. These flat fields are now really more productive than the rolling lands. By adding phosphoric acid to the soil the finest wheat in Indiana is grown on the flat lands to-day.

The soil is useful in proportion to its fertility, granted that the kind of crop that is suitable to the soil is grown. The farmers learned to recognize this fact, and where they formerly produced from 8 to 10 bushels of wheat per acre they are now getting from 30 to 40 bushels per acre.

The magnitude of the crop is determined chiefly by the amount of plant food available in the soil. I have studied this particularly in the case of one or two standard crops, especially in the case of the sugar beet. I find that of all the factors which go to make a rich sugar beet the soil is the least important, but of those which go to make a big crop of beets the soil is the most important. Aside from the principles which I have enumerated, of the natural selection of plants for soils, it is evident that the soil is improved under artificial conditions in proportion as it will produce larger crops, while under these same conditions the character of the crop is determined largely by what we call meteorological conditions. In the case of the sugar beet, granting that the soil will produce a standard crop, say 10 tons per acre, the

amount of sugar in the beets depends upon a great many conditions, particularly those of temperature and sunlight. It is necessary that there be sunlight, but not necessarily sunshine. Formerly I said "sunshine," but my investigations have taught me to say "sunlight." The rays which filter through the clouds are almost as useful as if they fell directly upon the plant; in fact in southern latitudes more so as cloudy weather is then an advantageous factor in diminishing the intensity of the heat. This factor is purely a meteorological one. We want plenty of light and an even low temperature to produce good sugar beets. We are studying the effect of meteorological conditions, sunlight, etc., on the gluten in wheat and its other nitrogenous constituents. It is not the soil which determines the amount of gluten or nitrogenous matter in wheat. A long period of growth tends to diminish the nitrogenous content of wheat and increase the starch content. Wheats that are sown in the springtime and harvested within a few months are richer in nitrogen and poorer in starch than wheats planted in the autumn and harvested the next season.

Scientific agriculture, in the progress of agricultural chemistry, is now endeavoring to show the practical farmer what meteorological conditions control the character of his crop, and what soil conditions control the magnitude of his crop, and thus teach him to change its constituents in such a way as to produce those things which are most useful and valuable and in the greatest quantities. In other words, agricultural chemistry, having determined what the soil is, what plants are, and how fertilizers can be made and applied, is now advancing to a still higher plane of investigation to determine how the soil shall be made maximum in production and how the conditions of growth shall secure the maximum of desirable qualities.

The PRESIDENT. If there is no objection, we will take up the subject of sugar. Two papers were presented yesterday. There will be opportunity for discussion.

Mr. WILEY. I would like to say a word of further explanation to some of the members who have adhered to the action of the international committee on sugar analysis. The chairman of this committee, Dr. Herzfeld, has secured by circulars the names of chemists throughout the world who have signified their adhesion to the conclusions of the committee. The purpose is to publish the names from all countries very soon in the Zeitschrift des Vereins der Deutschen Zucker-Industrie, of which Dr. Herzfeld is the editor. I would be glad if the members of this association who are interested in sugar analysis and who have not received that circular would apply for one, so that their names can be inserted in the proof sheets. The object of this publication is to make known those who have adopted the principles which are set forth in the action of this international committee. The committee will meet again in Berlin in June and probably will then be

discharged. Of course, we hope to have a large representation from our country, and I think we shall. This report is not a detailed one. It leaves the matter of details to the various associations throughout the world. It has established certain principles in polarization and estimation of sugars. While it may be true that the principles which this committee has adopted are not altogether the best, it is certainly true that they will secure a uniformity of procedure throughout the world.

Other international committees have been appointed for other purposes, and among them is a committee for the establishment of a uniform international method for the analysis of fertilizers. This committee has also reached a general agreement and has adopted as one of the bases of action our own official methods. The adoption of these general principles will go far toward securing uniformity of practice, and a most important step has been taken. An international committee on analytical chemistry has also been appointed, and will hold its first meeting next June, at the time of the assembly of the Fifth International Congress of Applied Chemistry at Berlin. Professor Lunge, of Zurich, Switzerland, is president of the committee. We have on this committee representatives from all parts of the world, making it international.

I must say with some pride that we were the first to attempt to secure uniformity of methods. I believe this whole movement for the unification of methods has sprung from the agricultural chemists of our country. England in most things is a progressive country, but she has made the least progress in this particular, and has but rarely had a representative at the international congresses of applied chemistry. There is one step in the way of uniformity for which the English agricultural chemists deserve credit, that is the adoption of a condenser, modeled after our own, for the determination of volatile acids on dairy products. So even England has taken one step in the direction of uniformity.

The PRESIDENT. I would like to ask if this list of the adherents to the conclusions of the international sugar committee is to be published as a separate report?

Mr. WILEY. I do not think it will be, but we may be able to get separate lists, and when the proof comes of the names of the adherents in this country I will write to Dr. Herzfeld for copies for those who are subscribers, or will endeaver to have the list published in the journal of the American Chemical Society.

The PRESIDENT. In the absence of the referee on tannin, the question of food standards is now before us for discussion. We have the honor to have with us to-day Mr. Hamilton, secretary of agriculture of Pennsylvania, and we shall be glad to hear from him.

REMARKS ON FOOD STANDARDS.

By Mr. John Hamilton,
State Secretary of Agriculture, Pennsylvania.

I was unfortunate in not being here to-day to hear the report which was presented to the association on food standards, and therefore I am not informed as to what has been done. I know that last year certain things were agreed upon, but I have seen no publication of the results. I am not sure whether the committee adheres to the things which were agreed upon then, or whether, in the natural progress of things, changes have been suggested, so that they are still holding these matters in suspense. Those of us who are actively engaged in the work of securing purity of foods for the people in our several States are greatly interested in the work of this association, because the questions that are involved are questions of a scientific character, of a character that can not be determined by the ordinary physician or practitioner in the several States. I am glad to know that this association has taken up the question of food standards in a way that is likely to give the people who have charge of this work an authority which can be quoted in the enforcement of the laws and information that will be reliable. The great difficulty that is encountered by the food officers is that of getting accurate information. Experts disagree with regard to certain facts in our food work, and so when we come into court we find that men of attainments hold certain opinions in regard to the use of food preservatives and coloring matters, while other food experts, graduates of the same school of medicine, are found upon the other side confronting us, before a jury, with their testimony which is exactly contrary to that we have presented. So there is confusion and each case has to be fought out on its own merits, and sympathy for the defendant often determines the action of the jury to the injury of the public. There is need for accurate information that will be accepted and agreed upon by all scientific men with regard to this question of standards, and with regard to the healthfulness or unhealthfulness of food preservatives and coloring matters.

There are three difficulties with which the food authorities have to contend. The first is in obtaining uniformity in methods of analysis. One of the great objects, I suppose, of this association is to secure this uniformity, and it has succeeded in bringing about a great change in this respect, so that substances which are now sent from one chemist to another are likely to correspond in their analyses. But I do not understand that all of the food analysts are entitled to become members of this association, and, therefore, some of the chemists that are now employed in the States are still pursuing methods that have been rejected by this association. Consequently there is discrepancy in their results. If the association could take into its membership food analysts of the several States, it seems to me that it would be a great benefit to those of us who are now trying to enforce the law, for then our analysts would agree in their testimony.

There is another matter of great importance—the question of what shall constitute a standard of purity; how each chemist may know when the substance is of the proper standard. If such a standard was ascertained and adopted for the several States, it would be a great advantage to the manufacturers in their work of preparing food, and there would be a great simplification of the work of the food commissioners in the enforcement of the law. In the State of Pennsylvania we took up this question and did the best we could with it. It was an immediate necessity that some standard should be adopted. We had to meet the question at once and it seemed that we were not likely to get the information from other sources soon, so we called a meeting of all of the food analysts in the State department of agriculture, securing also expert pathologists and others not connected with the department who were interested in the matter of purity of foods, and presented before this

meeting the question of standards, and also that of the effects of antiseptics, preservatives, and coloring matter. There were united in that meeting lawyers and scientists, some of the most able men that we have in our State, and we formed a set of rules that we have since used in the prosecution of our work. I will read one or two to give you some idea of what has been done:

1. All foods manufactured, sold, offered, or exposed for sale are held to be represented as pure, unless accompanied by adequate notice to the contrary, in which case they must be distinctly labeled as "mixtures" or "compounds," or as "artificial" preparations.
2. Food sold as pure must be true to name, of standard strength, quality, and purity, and not a compound, mixture, or an artificial preparation or imitation.
3. Where no standard of strength, quality, or purity is fixed by law, the standard required shall be that adopted by the highest recognized authorities, such as the United States Pharmacopœia or the Association of Official Agricultural Chemists.
5. No fraudulent or worthless article, having little or no food value, shall be mixed with standard goods or substituted for them, and be sold as food under the label "compound" or "mixture;" but all foods sold under this designation must be composed of substances recognized as "ordinary articles or ingredients of articles of food."
6. The question of the admissibility of a nonpoisonous or harmless foreign substance in a food may depend upon whether the substance introduced is necessary in order to improve the value or quality of the food, or is fraudulently added as a diluent and cheapener.
7. No food shall be sold under the name of a substance of which it contains none or only an inconsiderable quantity, and when a name is "coined" therefor such name shall not be suggestive of any substance not contained therein.

The wording of the food laws in force in the several States is practically the same. We have held that where the quantity of the component parts of a food or its quality is not fixed by law the standard shall be that adopted by the American Association of Official Agricultural Chemists or by the United States Pharmacopœia. So we look to you for information, and when a case comes into court, and the declaration is made that a certain standard is held by your association, it should be accepted as evidence, the best that could be secured.

We have also another rule, No. 4, that "no food shall have added to it anything that is poisonous or injurious to health," no matter how small the quantity of the poisonous or injurious substance used. The supreme court of our State has sustained us in this position.

We have another rule of importance—I am reading only those which are likely to be especially interesting to you—which permits the "use of a moderate quantity of coloring matter which is not poisonous or injurious to health, provided the goods are otherwise pure and of standard quality."

We were recently confronted with the question as to what we should do in regard to the use of salts of copper in the coloring of vegetables. We have ruled against their use. One purpose of my visit here is to discover what this association holds with regard to the use of these salts; whether they are poisonous and therefore injurious to health or whether they shall be permitted. The question was a practical one with us and we had to answer it at once. We must have evidence that will sustain us. We have always made it a rule in our State to give the public the benefit of the doubt in such cases, when there is any doubt, and to place the responsibility of permitting the use of these doubtful substances upon the courts. It seems to me that a declaration coming from this body on this subject would have great weight. If there is a question as to whether a substance is injurious to health or not, we hold that it is injurious to health, and it remains for those who wish to force it upon the public to show that it is not.

I am glad to know that your committee on food standards is making progress, but it seems to those of us who have to decide upon such questions every day that it is a little slow. If the matter can be hurried a little it will be a great advantage to those who are engaged in enforcing the laws of the several States.

I have also another matter which I wish to call to your attention. I refer to the position we have taken in the matter of the use of preservatives. We are holding that borax, salicylic acid, and other similar substances, such as formaldehyde and benzoic acid, are injurious to health and ought to be prohibited. Food can be preserved without their use and therefore they are wholly unnecessary and should be excluded. I will read our ruling, so as to give you an idea of our position on the question of the use of preservatives:

12. Articles of food that can be prepared by the use of improved processes, so as to preserve them from decay or change, shall have no preservative added, other than salt, sirup, sugar, saltpeter, spice, vinegar, or wood smoke

When we have no law that is specific or that gives us authority to designate or fix standards, we hold that if these standards are formulated in a common-sense way the courts will sustain them, and although not statute law they will be interpreted in accordance with the maxim that "the safety of the people is the supreme law." Thus far we have been sustained in the definitions we have made and yet each time we come into court we have to meet the same set of experts, hired by the manufacturers to confront us, and have the same battle to fight over and over.

I think that no more important question is now before us than this question of the proper preparation of food for the consumption of our people. The amount of adulteration is very great. I had occasion in preparing a paper the other day to go over the work of our department for the last two years. Our chemists had analyzed 5,000 samples of food, and over 50 per cent of this food was found to be adulterated in some form, so that the amount of adulteration is still very great, notwithstanding the efforts that have been made to exclude these goods from the markets. I feel that this association ought to disclose, as soon as it safely can, what it has done toward fixing standards and determining the character of preservatives, because the information is so very much needed, and, if we wait until the whole plan is perfected, we shall wait, perhaps, too long, and bring into discredit the work of the food commissioners in the several States, who had to define their position and could not delay.

I want to say to any of you who have ambitions, in a political way, "Don't ever be a food commissioner." That will ruin you. It is the last step that a man takes in political life, if he is honest. A food commissioner needs to have the backing of the best scientific men. If he depends simply on his own information he will have no show in these days. As Secretary Wilson has just stated, one man can not know very many things nowadays; he must get his information from a large number of people, and the best he can do is to find people who know, and then send for them. I have tried to make use of this principle in our department, and accordingly have made use of this association in the preparation of bulletins on a wide range of agricultural subjects. The experiment station work throughout the United States, with which most of you are associated, has done good service to agriculture in general, because it has brought into use a large number of the best, most highly trained scientific minds that the country possesses, for the solution of those difficult questions which embarrass the agriculturist. I am gratified to be here to-day, and am only surprised that the secretaries of the boards of agriculture of all of the States are not here to get information as to what is being done in the line of their work. It certainly is one place to which they can afford to come and get in contact with the men who are out on the firing line of investigation; who are going into the fight and getting facts for daily use. The men who have the administration of agricultural affairs in the several States can not afford to be without this knowledge.

I understand that an appropriation has been made for the investigation of the use of antiseptics, preservatives, and coloring matters in foods. I think this is a most admirable beginning, but it needs to be established upon a broader basis, by the formation of a large board of experts, who shall give their undivided time to the investigation of these subjects. One man can not do much, but a large number of

specialists, united in a board, could take up these subjects, and much information could be obtained in a short time, and time is now of exceeding value, both to the consumer whose health is at stake and to the manufacturer whose money interests are involved.

I appreciate the great work that this association has been doing for agriculture, and the work that it is doing to establish the truth as it relates to the use of various preservatives in the people's food, many of which are certainly injurious to the public health. I am obliged to you for your courtesy in giving me this opportunity of calling your attention to the pressing needs of the food authorities who are intrusted with the enforcement of the laws enacted in the interest of the public health.

Mr. Eaton. The National Association of State Dairy and Food Commissioners appointed a committee last year at Buffalo to meet with this association to confer with its committee on food standards to see what aid could be given. The committee consisted of Dr. R. M. Doolittle, of Michigan; Dr. A. S. Mitchell, of Wisconsin; Dr. William Frear, of Pennsylvania, and myself. As I am the only one present, I wish to express my thanks for the courtesy shown me.

The President. I was about to call on Mr. Eaton. We certainly expected to hear from him in regard to this matter. Our constitution provides that analytical chemists connected with the United States Department of Agriculture, or with any State or National institution or body charged with official control of the materials named in section 1, are members of this association.

Mr. Van Slyke. I move that the report of the committee on food standards be approved and the committee continued.

This motion was adopted.

The President. If there is no objection we will proceed to the discussion of tannin. Is Mr. Krug present?

Mr. Krug. Last year we made quite a radical change in our work by entering on a new field. We had been working for a number of years on the analysis of extracts and barks and we concluded that that method was upon a safe basis, and then decided to take up the determination of the total acidity in tan liquors. The determination of the acidity is of considerable importance, because if the liquor becomes too acid it does not make a good leather. Neither does it make good leather when not sufficiently acid. I desire at this time to read the following letter received from Mr. Procter of the International Association of Leather Trades Chemists:

September 20, 1902.

Dear Dr. Wiley: As I suppose your A. O. A. C. convention will be coming on soon, I send you under another cover a copy of the Leather Trade Review, containing a report of the Leeds meeting of the I. A. L. T. C., instead of waiting for a more official version. You will be pleased to see that we have made a great step toward coming into agreement with the A. O. A. C., your chrome shake method now being permissive, as well as the use of 590 or any other paper. I hope you will see your way to meet us in adopting the same mode of correction for the absorption of tannin in filtration, of which you will have seen fuller details in the Collegium. Of course if you prescribe a definite mode of filtration, there will be no difficulty in fixing also

a definite correction applicable to all the ordinary materials, sulphite extracts being generally the only ones requiring a special value, and the whole correction with 590 being a very small one.

As regards our permissive adoption of the A. O. A. C. method, the decision was based on experiments which have not yet been published in full, which showed, that adopting the results of any of the hide powder methods as a standard for that particular method, the results of the filter method with comparatively pure tannins (gallotannic acid, quebracho) could be raised by nearly 100 per cent by the addition of nontanning matters, such as gallic acid, to the solution. Your method gave truer results, but was itself liable to errors of 50 per cent or more, so that it can only be considered as a temporary expedient, and further experiment is eminently desirable to find one less affected by the presence of impurities, and especially of acids. Your method of preparing chromed powder, though all right where large numbers of analyses are made daily, is very troublesome for chemists who only have such work occasionally, and improvements are urgently wanted either in the direction of abridging the necessary washing, or making a powder (either dry or moist) which will keep and act reliably. I am not sure that formaldehyde may not be satisfactorily substituted for chrome in the preparation, and this would much diminish the required washing. We are experimenting in this direction, but do not wish at all to limit others in also taking up the same work. * * *

With kind regards.

Yours, very truly, H. R. Procter.

Mr. Krug. With reference to the statements made by Mr. Procter concerning the time lost in preparing chromed hide powder when a chemist makes only a few analyses at a time, I want to say that it is perfectly feasible to make up a considerable quantity at a time, removing as much water as possible and placing it in a tightly stoppered bottle with formaldehyde, when it will keep as long as six months. In regard to the other points which he discusses, I hope that the referee for next year will take up a comparative study of the changes suggested and decide if their adoption is desirable.

Mr. Wiley. I have the honor to be a member of the International Association of Leather Trades Chemists. I have, however, attended only one meeting, but hope to attend others. Only European countries are represented. What we want to do, if possible, is to get one of those gentlemen to come over to our meeting and to send Mr. Krug to one of their meetings. There is no doubt of the fact that they want to meet us on common ground. If we send a representative, there would be no difficulty, in my opinion, in securing a perfectly uniform method of analysis, but at the meeting which I attended it was easy to see what the trouble was. There was no one there who had a knowledge of the work except Mr. Procter, who has been president of this association and is an authority on this subject of world-wide reputation. He is thoroughly in earnest in his desire to cooperate with us. I am glad he has approached this association again, and I am sorry that the proceedings which he sent did not reach us. I would suggest on the part of this association that we answer

Mr. Procter's letter and ask him if he can not send a delegate to our meeting or have their delegate confer with ours. I would therefore ask authority to make such a proposition to Mr. Procter in my reply to his letter.

Mr. KRUG. I move that such authority be granted.

The motion was adopted.

[NOTE BY THE EDITOR.—In accordance with the above instructions the following letter was sent to Mr. Procter:]

DECEMBER 12, 1902.

Prof. H. R. PROCTER,
Leather Industries Laboratories, Yorkshire College, Leeds, England.

DEAR PROFESSOR PROCTER: Your letter of September 20, in regard to our official methods on tannin, was read before the meeting of the Association of Official Agricultural Chemists in October. I was instructed by motion at that meeting to make a proposition to you looking toward a conference between a delegate from our association and the International Association of Leather Trades Chemists. We should be glad to have your delegate attend the next meeting of our association, and perhaps it could be arranged to have a delegate from the A. O. A. C. attend your next convention. I shall be glad to receive any suggestions from you, as it would seem that only in some such way can a perfect understanding be reached and any satisfactory degree of uniformity attained.

Very respectfully,

H. W. WILEY,
Secretary A. O. A. C.

The PRESIDENT. The report of the referee on foods and feeding stuffs is now in order.

REPORT ON CATTLE FEEDS.

By C. A. BROWNE, Jr., *Referee.*

OUTLINE OF WORK.

The work this year on feeding stuffs was practically along the lines followed by preceding referees. In response to a circular letter inviting cooperation in the work favorable replies were received from eighteen chemists, and to these the following samples were sent:

No. 1. Timothy hay.

No. 2. Distiller's grains.

The sample of hay was drawn from a lot of pure timothy used the past winter for the steer-feeding experiments in the respiration calorimeter at the Pennsylvania experiment station. The distiller's grains were kindly supplied by the H. J. Heinz Company, of Pittsburg, and consisted mostly of the hulls and residues from a corn mash.

The suggestions made by last year's referee, Mr. Krug, were made the basis of the work, which comprised the following:

Determinations of moisture, fat, and pentosans on both samples according to the official method.

Determinations of crude fiber in both samples according to both the official and König methods.

If any time remained for further work after completing the above, it was suggested that a determination of starch be made in the distiller's grains by the diastase method and also a determination of sugars (sucrose and reducing) in the timothy.

In spite of the fact that the early date of this year's meeting shortened the time at the disposal of the reporters and prevented many of them from doing all the work, considerable interest was manifested and reports were obtained from nine chemists.

ESTIMATION OF MOISTURE.

Notable discrepancies exist in the moisture determinations, but these are to be explained partly by differences in the method of drying.

TABLE I.—*Moisture determinations.*

Analyst.	Method of drying.	Timothy hay.	Distiller's grains.
		Per cent.	*Per cent.*
E. B. Holland, Massachusetts	Glycerin and water oven, 100° C	9.14	8.35
T. M. Price, Maryland	Water oven	8.85	8.40
F. W. Woll and G. A. Olson, Wisconsin.	Water oven, 5 hours	9.16	8.40
L. A. Hill, New Hampshire	Water oven, atmosphere of CO_2	9.43	8.85
C. A. Browne, jr., Pennsylvania.	Water oven, 5 hours, 98° C	9.32	8.49
S. D. Averitt, Kentucky	do	9.50	8.75
Do	Caldwell tubes in H, 5 hours, 98° C	9.99	9.24
Do	Caldwell tubes in H, 10 hours, 98° C	10.16	9.42
R. W. Thatcher, Washington.	Caldwell tubes in H, 7 hours, 98° C	10.00	9.42
J. H. Norton, U. S. Dept. Agr.	Air bath to constant weight, 7 hours, 100° C	10.35	9.30
Do	Air bath, 5 hours, 100° C	9.72	9.22
Do	Water oven to constant weight	8.98	8.39
Do	Vacuum, 100° C., 5 hours	9.20	9.07
A. W. Bosworth, Rhode Island.	Watch glasses in H, 5 hours, 98° C	8.25	8.37

In the results of Mr. Averitt the maximum loss on drying in air was obtained in five hours, after which there was a slight gain in the case of both substances; by the method of drying in hydrogen the materials also began to increase slightly in weight after ten hours' drying.

The Caldwell method of drying in hydrogen gave very concordant results so far as it was tried. The results obtained by drying in an air bath to constant weight at 100° agree closely with those obtained by the Caldwell tubes. The high results obtained by these two methods clearly show that all the moisture is not removed by the ordinary method of drying in a water oven for five hours. This fact was brought out ten years ago at the ninth annual convention, so that, to quote one of the chemists, "we are thrashing over old straw by opening up this question again."

It does not seem desirable to prescribe one fixed method for the determination of moisture in feeding materials. No method of drying in air at 100° would answer for materials containing easily oxidizable oils, such as linseed meal; in such cases the Caldwell method is to be recommended. On the other hand, the method of drying in hydrogen at 100° C. would not answer for materials containing levulose or invert sugar. In such cases the method of drying in vacuo at 70° C., proposed by Carr and Sanborn[a] in the proceedings of the twelfth annual convention of this association, seems to be the only practicable one. In the choice of a method the chemist must be guided by the nature of the material to be analyzed.

[a] U. S. Dept. of Agr., Division of Chemistry, Bul. 47, p. 134.

ESTIMATION OF ETHER EXTRACT.

TABLE II.—*Ether-extract determination.*

Analyst.	Timothy hay.		Distiller's grains.	
	Original sample.	Water-free basis.	Original sample.	Water-free basis.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
E. B. Holland, Massachusetts	[a]2.00	[a]2.20	[a]6.21	[a]6.78
T. M. Price, Maryland	1.87	2.05	5.78	6.31
S. D. Averitt, Kentucky	2.01	2.23	6.50	7.17
F. W. Woll and G. A. Olson, Wisconsin	2.02	2.22	6.58	7.18
R. W. Thatcher, Washington	2.44	2.71	6.59	7.27
L. A. Hill, New Hampshire	1.93	2.13	6.20	6.80
A. W. Bosworth, Rhode Island	1.84	2.00	6.41	6.99
M. H. Pingree, Pennsylvania	1.94	2.14	6.13	6.69
Average	2.01	2.21	6.30	6.90

[a] Results, after deducting blank of 0.44 per cent for extract from new capsule, cotton, apparatus, and ether, were 1.56, 1.72, 5.77, and 6.29. It is not customary to make corrections for a blank in determining ether extract, as was done by Mr. Holland, and this seems a point worthy of attention. We may have here an explanation of some of the discrepancies observed between the results of the different chemists.

In a current number of the Chemiker Zeitung[a] Beger calls attention to a deficiency in the ordinary method of fat determination, the point being that the fat is not completely extracted from certain materials, especially such as are high in protein. To obviate this difficulty Beger recommends the use of the pepsin process first advocated by Dormeyer[b] and afterwards studied by Nerking in the analysis of meats. Nerking[c] showed that with dried meats the customary extraction with ether is insufficient to remove all the fat, but that if the material is first subjected to a digestion with pepsin solution the fatty albuminoid compounds are broken up and the fat may then be completely removed by means of ether. Beger has studied this method in its applicability to many feeding materials, and the following figures are taken from his article:

TABLE III.—*Ether extract—digestion with pepsin solution (Beger).*

	Rice gluten.	Brewer's grains.	Malt sprouts.	Bran.	Linseed cake.	Cotton-seed meal.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
Ether extract, extraction for 12 hours	0.85	8.52	1.82	5.12	9.07	10.02
Ether extract, second extraction for 12 hours	.40	.10	.32	.03	.28	.05
Ether extract after digesting residues with pepsin and again extracting	5.74	1.14	.75	.25	.31	1.09

Results obtained with a number of other materials are also given. In all cases an additional quantity of fat was obtained after digesting the extracted residues with pepsin, the amount in some cases, as with the rice gluten, being very marked. Beger states that digestive coefficients of the fat in rice gluten gave negative values according to the ordinary method of ether extraction, while by the Dormeyer method a

[a] 1902, **26**, No. 11.

[b] Pflügers, Archiv. für Physiologie, **61**, 1895, p. 341; ibid., **65**, 1896, p. 90.

[c] Pflügers, Archiv. für Phys., **85**, 1901, p. 330.

positive result was obtained. Physical and chemical tests of the fat extracted after the pepsin treatment showed it to have the same properties as the ordinary fats.

Your referee has not been able in the limited time at his disposal to give this method a trial; it would seem, though, that we ought to make a study of this method upon a few of our typical feeding materials. The results might show the necessity of revising the digestive coefficients of fat in some of our feeding stuffs. By subjecting the residues from the ordinary ether extraction to the pepsin treatment the two methods can be easily compared without much extra trouble.

The method of treatment is as follows: Three to five grams of substance are digested with one gram of pepsin, Merck (this is found to be free from ether extract), dissolved in 480 cc water and 20 cc of 25 per cent HCl at 37° to 40° C. for twenty-four hours. The residue is then filtered on a Gooch crucible, washed several times with cold distilled water, and then, after drying, extracted with ether in the usual way. The filtrate must also be shaken out with ether several times and the extract from this united with that from the dried residue.

Estimation of Crude Fiber.

At the last meeting of the association Mr. Fraps presented a paper upon the determination of pentosan-free crude fiber by the König method, with the suggestion that the study of this method be taken up by the association. This suggestion was acted upon, and a comparison of the results obtained by the official and König methods upon the two samples sent out is given herewith. The results by both methods exhibit considerable variations and show that the determination of fiber is at present in a most unsatisfactory condition, as indeed it always has been. The results on timothy hay by the official method, especially, show extremely wide and unaccountable variations. There seems to be no determination where the element of personal equation is so pronounced as in that of crude fiber.

Table IV.—*Determination of crude fiber.*

Method and analyst.	Timothy hay.		Distiller's grains.	
	Original sample.	Water-free.	Original sample.	Water-free.
OFFICIAL METHOD.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
E. B. Holland, Massachusetts	37.41	41.17	19.93	21.72
	37.40	.....	19.80	.....
T. M. Price, Maryland	42.10	46.19	13.53	[a]14.77
S. D. Averitt, Kentucky	35.32	39.04	19.51	21.65
	34.83	.....	19.71	.....
F. W. Woll and G. A. Olson, Wisconsin	40.70	.....	20.18	.....
	40.25	44.45	21.48	23.28
	40.20	.....	22.33	.....
L. A. Hill, New Hampshire	34.77	38.24	18.40	20.20
	34.50	.....	18.41	.....
R. W. Thatcher, Washington	42.40	46.82	23.64	25.79
	41.87	.....	23.07	.....
A. W. Bosworth, Rhode Island	36.25	39.55	20.43	22.10
	36.33	.....	20.07	.....
M. H. Pingree, Pennsylvania	35.44	38.91	19.18	[b]21.36
	35.12	.....	19.93	.....
J. H. Norton, U. S. Department of Agriculture	35.14	39.19	19.57	21.57
Average	.....	41.51	.....	22.21

[a] Results omitted from average.
[b] Fiber contains 0.28 per cent N=1.75 per cent protein.

TABLE IV.—*Determination of crude fiber*—Continued.

Method and analyst.	Timothy hay.		Distiller's grains.	
	Original sample.	Water-free.	Original sample.	Water-free.
KÖNIG METHOD.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
E. B. Holland, Massachusetts	31.69	34.44	21.49	23.27
	30.90	.....	21.17	.....
T. M. Price, Maryland	21.15	.....	.....	.....
	24.83	[a]22.73	.....	.....
	16.18	.....	.....	.....
S. D. Averitt, Kentucky	25,20	[a]26.32	14.60	[a]17.23
	22.10	.....	16.61	.....
F. W. Woll and G. A. Olson, Wisconsin	32.00	.....	24.31	.....
	33.10	35.85	23.51	26.08
	32.62	.....	23.85	.....
L. A. Hill, New Hampshire	31.68	35.11	20.32	22.11
	31.91	.....	20.00	.....
R. W. Thatcher, Washington	32.94	36.79	25.01	27.61
	33.27	.....	.....	.....
A. W. Bosworth, Rhode Island	32.83	35.78	22.11	24.22
	32.83	.....	22.27	.....
C. A. Browne, jr., Pennsylvania	[b]31.68	34.89	[c]22.24	[d]24.60
	31.60	.....	22.81	.....
J. H. Norton, U. S. Department of Agriculture	31.15	34.75	21.21	23.38
Average	.....	35.37	.....	24.47

[a] Results omitted from average.
[b] Fiber after boiling with 1.25 per cent NaOH is 27.49 per cent.
[c] Fiber after boiling with 1.25 per cent NaOH is 17.78 per cent.
[d] Fiber contains 1.09 per cent N=6.81 per cent protein.

COMMENTS OF ANALYSTS.

This being the first general trial of the König method, it is thought well to give the comments of the different analysts in full:

E. B. Holland.—Considerable difficulty was experienced in the filtration, linen being used for the purpose. The final product, even after prolonged washings with hot water, alcohol, and ether, was not as clean as desired.

T. M. Price.—König's method for crude fiber I did not find satisfactory, as it was impossible to get concordant results with duplicates.

S. D. Averitt.—Much difficulty was had in filtering the fiber obtained by the König method. It was necessary to dilute the liquid with water and allow the fiber to settle before it could be filtered, and even then the process was very slow. If the filtration is always as difficult as we found it, the method can hardly be considered practical.

F. W. Woll.—The filtration by the König method took from 1 to 10 hours. To help along the filtration in one determination, the mixture was diluted with hot distilled water after boiling, and the filtration then took only 8 minutes.

R. W. Thatcher.—König's method for crude fiber is a very satisfactory one as far as ease of manipulation and agreement of duplicates is concerned. It gives results that are in no way comparable with those obtained by the official method, however. Some difficulty was experienced in filtering in the determinations made on the distiller's grains, the first sample being ruined in the attempt. In the case of the second sample the method of filtration outlined in the accompanying note (p. 154) was used with very satisfactory results, although filtration was slow even with this method of procedure, the material being not wholly removed from contact with the glycerol-

sulphuric acid for nearly an hour after the filtration was begun. This is not a serious objection to the König process as compared with the official method, however, since in the latter even more difficulty was experienced in filtering off the alkaline extract.

A. W. Bosworth.—In the König method for crude fiber, after digestion with the glycerol-sulphuric acid, I had a great deal of trouble in filtering. The timothy hay took between six and seven hours to filter and wash.

J. H. Norton.—Fiber by the König method was filtered in a funnel with a 2-inch porcelain plate and asbestos, no platinum being available. The timothy hay gave trouble, as it was so loose as to allow it to suck through with some asbestos. In each case the washing was continued until the liquid came through clear. Attempt was made to filter the distiller's grains the same as the hay, but the filter clogged and had to be transferred to a 3-inch Hirsch funnel with asbestos. Alcohol seemed to have a greater solvent effect than ether and alcohol. The fiber from the distiller's grains gave trouble in burning on account of the large quantity of asbestos it was necessary to use.

COMMENTS OF REFEREE.

The claim that the König method is shorter than the official method does not seem to be realized by all the chemists, the complaint of the difficulties in filtering, where the König process was used, being very general. Your referee has found the use of a flat-bottomed perforated porcelain funnel, the kind designated in German laboratories as a "Nutsche," and listed in our catalogues as a Büchner funnel, very convenient for difficult filtrations. By using a filter of linen or of hardened paper and by first diluting the hot glycerol-acid mixture with boiling water, the filtration and washing by the König method, employing such a funnel as the one just described, occupied not over ten minutes. The most serious objection to the König method, as it now stands, in the opinion of your referee, consists not in the difficulty of filtration, for that may be in a great measure prevented, but in the danger we run of obtaining an impure quality of fiber. The fiber is, to be sure, practically free from pentosans, and a distillation with hydrochloric acid gives only traces of furfurol, but the boiling glycerol-sulphuric acid mixture does not effect, on the other hand, anywhere near a complete removal of the albuminoid matter in materials high in protein. It will be noted in Table IV that a lower percentage of fiber was found by the König method with the hay, while with the distiller's grains the König method gave in most cases several per cent more fiber. This is undoubtedly due to the high percentage of protein left in the fiber obtained by König's process, this containing in one case 1.08 per cent nitrogen, equivalent to 6.81 per cent protein. The official method also does not give us a fiber absolutely free from albuminoids; it is, however, much purer in this respect than the fiber obtained by the König process, the amount found in the fiber from the distiller's grains by the official method in one case being 1.75 per cent, about one-fourth that obtained by the König method.

Your referee believes we would experience this difficulty with the König method on all feeding materials high in protein, so that we would have little to gain by adopting a method which, while securing greater accuracy on one side, incurs still greater errors on another. As Mr. Thatcher observes, the two methods give results that are in no way comparable. The difficulty may, perhaps, be obviated by modifying the method of König, so that it will include a treatment of boiling the fiber with alkali as with the official method. Your referee has made determinations of the fiber in the two samples, using such a modification of the König method, and obtained 27.49 per cent fiber for the timothy hay and 17.78 per cent for the distiller's grains, results several per cent lower than those obtained by the simple boiling with the glycerol-sulphuric acid mixture. The resultant fiber was much whiter after boiling with the alkali; it contained 1.45 per cent protein and seemed to be nearly free from lignin, as well as from pentosans.

Your referee would recommend a further study of the König method for next year, with the additional treatment of the fiber with alkali as by the official method. We may be able in this way to arrive at a better method of estimating fiber. It does not seem right to throw the matter up without further trial. The results on timothy hay show that seven chemists obtained results by the König method agreeing within nearly 2 per cent, something that can not be said of the official method. Your referee does not believe that the König method as it now stands should be adopted by the association.

Estimation of Pentosans.

The results on pentosans, so far as reported, are presented herewith:

Table V.—*Determination of pentosans.*

Analyst.	Timothy hay.		Distiller's grains.	
	Original material.	Water-free basis.	Original material.	Water-free basis.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
E. B. Holland, Massachusetts	23.69	26.23	21.24	23.18
L. A. Hill, New Hampshire	21.94	24.22	21.95	24.08
A. W. Bosworth, Rhode Island	24.71	26.93	22.07	24.09
C. A. Browne, jr., Pennsylvania	24.61	27.14	21.99	24.01
J. H. Norton, U. S. Department of Agriculture	23.58	26.30	21.00	23.15
Average	23.71	26.16	21.65	23.70

By way of comment, Mr. E. B. Holland says: "Not being in favor of the new suggestion as to the amount to be taken, 3 grams were used as usual. The phloroglucol used was Mercks chemically pure, and the solution was prepared in the proportion of 6.5 grams to 750 cc of 12 per cent hydrochloric acid."

Your referee would like to recommend at this point the adoption by the association of the new factors of Kröber for calculating pentosans.[a] The factors at present in use, worked out originally by Tollens and Krüger, are now really obsolete and should be discarded. As is stated in an abstract[b] in the last number of the Experiment Station Record[c] "the close concordance between the data given by Rimbach and Kröber indicates the correctness of the new figures." One principal objection to the present factors is that they can not be successfully applied to small amounts of phloroglucid, the subtraction of the figure 0.0104 from the calculated weight of furfurol frequently giving negative results.

Considerable study is being devoted to the subject of pentoses and pentosans in Germany just at present, as is seen by the numerous contributions of Tollens, Salkowski, Neuberg, and others. The recent discovery by Hammarsten of pentosans in the nucleo-proteids of the pancreas and in other parts of the animal organism has especially stimulated researches in this direction, more however, from the physiological side. Good workable methods have been devised for the qualitative separation of the pentoses from one another, use being made of the various substituted hydrazins, such as benzylphenyl hydrazin and diphenyl hydrazin, and successful attempts have been made toward using these reagents quantitatively. Your referee has

[a] Journal für Landwirthchaft, 48, 1900, p. 375–384.

[b] For fuller particulars concerning Kröber's factors see the original articles by Kröber, Journal für Landwirthschaft, 1900, p. 375; 1901, p. 7. Also articles by Tollens, Zeitschrift für angewandte Chemie, 1902, pp. 477 and 508, and Zeitschrift für physiologische Chemie, 1902, p. 239.

[c] Vol. 14, No. 1, p. 9.

employed the benzylphenyl hydrazin with success in isolating arabinose from different materials, and has a specimen of the arabinose benzylphenyl hydrazone which he has recently obtained from timothy hay. There is no reason why these and other newly discovered methods may not be successfully employed to increase our knowledge of the constitution of many feeding materials.

Estimation of Starch.

Only two chemists made reports upon starch, the others finding it impossible to do this part of the work from lack of time. The following results were obtained:

Table VI.—*Determination of starch, diastase method.*

Analyst.	Distillery grains.	
	Original material.	Water-free basis.
	Per cent.	*Per cent.*
E. B. Holland, Massachusetts	4.95	5.40
C. A. Browne, jr., Pennsylvania	2.17	2.37
Average	3.56	3.89

The distillery grains had the appearance of being well malted, and the microscope showed with iodin only traces of starch. In a similar sample of distiller's grains which your referee examined some years ago 2.66 per cent of starch was found; the pentosans were also determined just before and just after the malt digestion. Pentosans in residue before malt digestion were 22.16 per cent of the original substance, and after, 20.98 per cent; the difference, or pentosans removed by malt digestion, being 1.18 per cent.

Similar results are reported by Lindsey [a] upon corn meal, wheat middlings, and lupine seeds. There would therefore appear to be a danger that with materials high in pentosans small amounts of the latter may be dissolved during the malting process, being afterwards hydrolyzed and estimated as starch. A study of this point was made some years ago by the association, by determining the pentosans in the extracts after the malt digestion. This never seemed to show very much, principally for the reason, already indicated, that our present formulæ are not adapted to calculating small amounts of pentoses or pentosans. Applying Kröber's formula to the weights of phloroglucid would show an appreciable amount of pentosans in these extracts.

As an illustration of this, a quantity of xylose having been obtained from timothy hay, 10 mg (1 per cent of 1 gram) were distilled with hydrochloric acid and precipitated with phloroglucin as usual. The weight of phloroglucid obtained was 10.3 mgs. This corresponds to 14 mgs xylose (1.4 per cent of 1 gram), using Kröber's formula. The formula now employed gives a minus quantity.

To study better the effect of diastase upon the pentosans, the experiment was tried of first isolating the pentosans from other substances before beginning the digestion with malt. Several hundred grams of timothy hay were finely ground, washed first with cold dilute hydrochloric acid, then with water, and lastly with boiling alcohol. From the hay thus purified the pentosans were extracted with dilute soda, precipitated with alcohol, then purified and dried according to the method of Wheeler and Tollens.

[a] U. S. Dept. Agr., Division of Chemistry, Bul. 51, p. 91.

Working upon this material the following results were obtained:

	Per cent.
Pentosans removed by malt digestion (by inverting and determining copper reducing power)	[a] 28.56
Pentosans removed by water digestion alone (by inverting and determining copper reducing power)	[a] 21.42
Difference, or pentosans removed through diastase	7.14

The experiments were carried out together under exactly similar conditions. The time of digestion was six hours. The results would indicate that diastase seems to exert some solvent effect upon the pentosans, at least when isolated. This solvent action is, however, undoubtedly much diminished when the pentosans exist in combination with cellulose and lignin in cellular tissues. The error introduced into the starch determination with our common feeding materials, judging from the percentage of pentosans removed during the malt digestion, would probably rarely exceed 1 per cent.

RECOMMENDATIONS.

It is recommended that after the sixteenth line the method for determining pentosans be changed to read as follows, following the directions prescribed by Kröber:

The solution is made up to 400 cc with 12 per cent hydrochloric acid and allowed to stand overnight. The amorphous black precipitate is filtered into a tared Gooch through an asbestos felt, washed carefully with 150 cc of water in such a way that the water is not entirely removed from the crucible until the very last, then dried to constant weight by heating four hours at 100° C., cooled, and weighed in a weighing bottle, the increase in weight being reckoned as phloroglucid. To calculate furfurol, pentose, or pentosan from the phloroglucid, use the table by Kröber.[b]

Mr. BROWNE. I have a communication on filtration in determinations of crude fiber from Mr. Thatcher, which he authorizes me to read.

NOTE ON FILTRATION IN DETERMINATIONS OF CRUDE FIBER.

By R. W. THATCHER.

All analysts of food products, or feeding stuffs, are familiar with the difficulty which is often experienced in filtering off the acid and the alkaline liquids in the determinations of crude fiber by the official method of the Association of Official Agricultural Chemists. Hence I wish to suggest the following modification of the usual procedure, which I have found to give very satisfactory results:

Select a funnel of sufficient size to contain the entire bulk of the mixture to be filtered and fit into its point a small platinum filtering cone. Introduce enough ignited asbestos wool to fill the cone a little more than full. Upon moistening, the wool softens into a fluffy mass, which may be drawn down into a firm, close filter by suction. The mixture to be filtered is now poured into the funnel, with the usual care to avoid disturbing the asbestos layer, and suction is applied. The filtrate obtained in this manner has always been found to be free of suspended particles of fiber. Filtration is very rapid in all cases except when working with finely ground flour or spices, which tend to clog the filter and impede the flow of the filtrate. In such cases place the funnel in an ordinary jacket of boiling water or steam in order to secure hot filtration, transfer the entire mass to be filtered to the funnel, and apply the suction as usual. Filtration will then proceed at the desired temperature and without further attention from the operator, thus avoiding the two objections to

[a] Pentosans = dextrose×0.97×0.88. Stone Am. Chem. Jour., **13**, 73.

[b] See report of chairman of Committee B for factors. For table in full see "Journal für Landwirthschaft, **48**: 1900, pp. 375–384.

the use of the Gooch filter as recommended in the official method. After filtration and washing are complete, transfer the contents of the funnel to a platinum evaporating dish, rinsing the last particles of fiber from the funnel to the dish with a fine jet of distilled water. Evaporate off the water thus used, dry to constant weight, and complete the determination as usual. I prefer this mode of operation to the use of a paper filter, with correction for loss of weight sustained by the paper in a blank determination, as suggested by Winton,[a] for the reason that, in addition to the possibility of obtaining additional fiber from the paper used in the acid filtration, I have found that duplicate determinations of the correction to be applied do not always give concordant results, probably because of variations in the weight and composition of individual filters in any given pack of them. I have used the method outlined above for several years and upon a great variety of samples with uniformly satisfactory results. In the cases where filtration is slow it proceeds without attention from the analyst, thereby relieving the tediousness of the operation very materially.

Mr. Wiley. I have a paper from Mr. Parsons on foods and feeding stuffs, which I think should be presented at this time. Mr. Parsons regrets that he is not here to attend the meeting, and offers some suggestions in regard to the analysis of malt liquors:

SUGGESTIONS AS TO THE ANALYSIS OF MALT LIQUORS.

By Charles L. Parsons.

I have recently had occasion to make analyses of a large number of samples of beer in connection with legal work in this State where the question is not so much to determine the alcohol content as to prove the malt origin of the liquor under question. This makes a very complete analysis necessary, and I think that several important changes can be advantageously made in the methods which will insure much greater rapidity without sacrificing accuracy. I beg to submit the following suggestions:

Alcohol.

Discard the use of hydrometer altogether. The best made are not sufficiently accurate. Use the picnometer with thermometer stopper, and allow the use of any temperature from 15.6 to 25°C. according to temperature of atmosphere, the picnometer to be calibrated with distilled water at the same temperature. This may seem a radical departure and will be criticised, but a study of the coefficient of expansion of pure water and mixtures of alcohol and water[b] will show that with such dilute solutions of alcohol as are under consideration the error would be less than 0.01 per cent. This error is less than would result from evaporation due to capillarity around the ground-glass stopper if the picnometer is filled at 15.6°C. and then brought to room temperature to avoid condensation on the glass, is much less than would arise from the use of a hydrometer, and is fully as accurate as by calculation from the tables of Squibb.

Protein.

Boil down the beer taken to a small bulk, but not to dryness, after acidification with a few drops of sulphuric acid before the main quantity of sulphuric acid or potassium sulphate is added. This will do away with the foaming which is otherwise almost uncontrollable.

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[a] Conn. Agr. Expt. Sta. Report, 1898, p. 189, and Bul. 65, Bur. of Chem., U. S. Dept. Agri., pp. 58, 154, and 155.

[b] Makins, Jour. Chem. Soc., 99: 224, and Silbermann, Comptes Rendus, October, 1848.

PHOSPHORIC ACID.

The uranium acetate method, which is so extremely rapid, can be applied with accuracy to the beer ash if the ash is first moistened with concentrated hydrochloric acid and the acid evaporated in the water bath. I have made comparative analyses with the gravimetric molybdenum method and find that, if expressed in the customary terms of percentages of the beer taken, the method can be depended upon to the third decimal place with certainty. The end point of the titration is exceedingly sharp when the ash is used. If acetic acid is substituted for hydrochloric, or if, after evaporation of the acid the ash is heated much above the temperature of boiling water, part of the phosphates are not attacked by the uranium solution. Use 50 cc beer for the ash and a uranium acetate solution, one cc of which is equivalent to 0.01 per cent phosphoric acid.

SULPHATES IN ASH.

Incorporate a method for the determination of sulphates and allow the use of the regular gravimetric method and the photometric method of Hinds;[a] this latter can be applied to the same solution as is used to determine phosphoric acid after it has been acidified with hydrochloric acid. Hinds's own tables agree much more closely with the gravimetric than those of Jackson.[b] By using the uranium method for phosphates and the photometric for sulphates, these two determinations can be completed in about fifteen minutes after weighing the ash.

ASH.

Use 50 cc of beer instead of 25 cc in order to correspond with the determinations of phosphoric acid and sulphates.

FREE ACID.

Dilute 10 cc of the beer several times with distilled water, add phenolphthalein, and titrate with tenth normal sodium hydrate. The end point is sharp and agrees with that obtained by delicate litmus paper.

Mr. WILEY. I have just received a letter from Mr. Shutt, who regrets his inability to be present on account of an attack of appendicitis. He had hoped up to the last moment to come and fears by reason of his indisposition that he will not be able to serve as referee, but hopes to remain the associate, as at present.

The PRESIDENT. Is it the pleasure of the association to communicate through our secretary the best wishes of the association to Mr. Shutt?

Mr. BOSWORTH. I move that the secretary be instructed to communicate our best wishes to Mr. Shutt.

The motion was adopted.

[NOTE BY THE EDITOR.—The following letter was sent to Mr. Shutt in accordance with the above instructions:]

OCTOBER 9, 1902.

Mr. F. T. SHUTT,
Experimental Farm, Ottawa, Canada.

DEAR SIR: Upon the receipt of the unwelcome news of your illness, at the last annual meeting of the Association of Official Agricultural Chemists, I was instructed

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[a] Jour. Amer. Chem. Soc., **22**: 269. [b] Ibid., **23**: 799.

to extend to you the sympathy of that body, together with their regrets that you should be absent from the meeting, and their earnest wish for a speedy recovery. To this I would add an expression of my own personal regret and the hope that you are now on the road to recovery.

Sincerely,

H. W. WILEY, *Secretary A. O. A. C.*

Mr. VAN SLYKE. I move that we adjourn until 9.30 to-morrow morning.

The motion prevailed, and the meeting adjourned at 4 o'clock p. m.

THIRD DAY.

SATURDAY—MORNING SESSION.

The meeting was called to order by the president at 9.30 a. m.

REPORT ON INSECTICIDES AND FUNGICIDES.

By J. K. Haywood, *Referee.*

The work for this year upon insecticides and fungicides has consisted principally in testing various methods that have been gathered together in previous years.

Outline of Work.

The following circular letter was sent out to all the station chemists:

Dear Sir: Having been appointed referee on insecticides and fungicides by the Association of Official Agricultural Chemists, I desire to know if you will cooperate with Mr. Emery, the associate referee, and myself in the work.

The subject will be divided into six groups, as follows:

1. Potash and soda lyes and soaps.
2. Arsenical insecticides.
3. Copper in copper carbonate.
4. Cyanogen in potassium cyanid.
5. Formaldehyde in formalin.
6. Nicotin in tobacco and tobacco extracts.

Will you kindly let me know what group or groups you will be able to work upon, and oblige,

Yours, very truly, J. K. Haywood, *Referee.*

It was hoped that a seventh class, petroleum products, could be added, but the chemist who was to work upon this class has not reported any results.

Twenty-three replies were received to this letter, 15 favorable and 8 unfavorable. Including the referee, 16 signified their desire to cooperate in the work. Thirteen asked for samples of arsenicals, 7 for samples of copper carbonate, 5 for samples of potash and soda lyes and soaps, 5 for samples of formalin, and 5 for samples of tobacco extract.

Samples and copies of the methods of analysis[a] were forwarded to those who desired to cooperate, with the request that they first perform the analysis exactly as directed, then suggest any changes that they might think necessary to either expedite or render more accurate the method as outlined.

The following reports have been received: Nine on arsenicals, 4 on copper carbonates, 4 on potassium cyanid, 4 on soda lye, 2 on whale-oil soap, 5 on formalin, and 3 on tobacco extracts.

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[a] See Circular No. 10, Bur. of Chem., U. S. Dept. of Agr., "Methods for the analysis of insecticides and fungicides."

Paris Green.

The following table shows the comparative results obtained on Paris green by employing the methods of analysis referred to above:

Table I.—*Results of work done on Paris green.*

Analyst.	H_2O.	Total As_2O_3.		Soluble As_2O_3.		Soluble CuO.	Total copper oxid.	
		Method I.	Method II.	Method I.	Method II.	Method II.	Method I.	Method II.
	Per ct.	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*
L. H. Smith, Illinois	0.75	57.75	56.65	0.78	3.10	0.95	29.83	31.43
	.68	57.63	56.65	.78	2.85	.70	29.83	31.30
	.....	57.75	.....	.....	.....	.....	.....	31.43
	.....	57.50	.....	.....	.....	.....	.....	31.43
	.....	.....	.....	.....	.....	.....	.....	31.43
H. T. Beans, Idaho	.60	56.82	56.44	.38	2.06	.64	30.00	28.88
	.63	56.89	56.45	.41	2.08	.40	30.12	29.32
	.....	56.70	56.45	.....	.....	.....	30.08	29.45
	.....	56.89	.....	.....	.....	.....	30.24	.....
T. M. Price, Maryland	.61	56.75	57.16	.60	2.72	3.45	30.31	30.15
R. W. Thatcher, Washington	.41	57.08	56.21	.62	2.77	1.05	30.80	30.78
	.43	57.15	56.19	.65	2.22	.35	30.56	30.45
D. L. Cleaves, Massachusetts (Hatch).	.37	56.78	54.83	1.67	.....	.....	.....	30.71
	.40	57.02	54.83	1.63	.....	.....	.....	30.40
	.....	.....	.....	.....	.....	.....	.....	30.52
R. J. Davidson, Virginia	.63	56.73	56.61	.53	3.63	1.05	30.60	31.19
	.63	56.78	56.56	.54	3.63	1.05	30.60	31.40
	.....	56.76	.....	.....	3.63	.....	30.60	31.19
	.....	56.74	.....	.....	.....	.....	30.32	31.40
	.....	56.74	.....	.....	.....	.....	30.32	.....
	.....	56.74	.....	.....	.....	.....	30.32	.....
H. J. Warner, Bureau of Chemistry, U. S. Department of Agriculture.	.53	57.21	57.09	.73	3.87	.....	30.42	[a]30.97
	.....	57.09	.....	.77	.....	.....	.....	30.97
James Emery, Biochemic Division, Bureau of Animal Industry, U. S. Department of Agriculture.	.59	56.66	56.36	.95	.....	.....	30.10	30.45
	.57	56.66	56.66	1.00	.....	.....	30.35	30.45
	.....	.....	.....	.....	.....	.....	.....	30.78
J. K. Haywood, Bureau of Chemistry, U. S. Department of Agriculture.	.73	56.93	57.39	.74	2.94	.50	30.43	[b]30.73
	.60	57.16	57.04	.74	2.85	.50	30.43	30.73
	.....	57.16	57.17	.....	.....	.....	.....	31.17

[a] A determination of copper oxid by weighing the oxid gave 31.07 per cent.
[b] Determination of copper by electrolysis gave 30.87 per cent copper oxid.

COMMENTS BY ANALYSTS.

L. H. Smith.—In the determination of soluble copper oxid the precipitate was not burned with powdered sulphur.

H. T. Beans.—In Method II, for total arsenious oxid, it is much shorter and just as accurate to standardize the iodin solution against a solution of arsenious oxid made by dissolving chemically pure arsenious oxid in a hot solution of sodium bicarbonate.

D. L. Cleaves.—In the determination of total copper oxid by Method I, no matter how much sodium thiosulphate was added, no end point could be obtained. In the determination of total arsenious oxid by Method II it was impossible to obtain a clear solution with hydrochloric acid.

R. W. Thatcher.—Method II, for total arsenious oxid, is in my opinion a very excellent one for work with samples of pure green, but unfortunately the cold dilute

hydrochloric acid used in dissolving the green does not completely dissolve any crystals of free arsenious oxid that may have been added. My experience is that such adulteration is by no means so uncommon as to warrant the adoption of a method which will fail to include free arsenious oxid in the total as determined by it.

The following comparative determinations of the total arsenious oxid in some commercial samples of paris green received for analysis at this laboratory were made at the same time that the above work was done:

TABLE II.—*Comparative determinations of total arsenious oxid.*

Sample.	Total arsenious oxid.		Soluble arsenious oxid, Method I.
	Method I.	Method II.	
	Per cent.	*Per cent.*	*Per cent.*
1	56.32	56.33	0.68
2	56.60	56.58	.70
3	56.71	56.20	.84
4	61.25	52.23	10.89
5	62.24	50.37	12.16

DISCUSSION OF RESULTS.

The figures in Table I for the amount of arsenious oxid by Method I show that the agreement between the figures obtained by each analyst and the agreement between the work of different analysts are most excellent. In fact, there are few of our methods which would give better results in the hands of different chemists working upon substances containing such large percentages of the component to be determined. It is true that one set of results is slightly higher than the rest, but they are very little higher, and this could very easily arise from a difference of 0.2 cc in the burette reading.

In the third column are given the results obtained by Method II for total arsenious oxid. It will be seen at once that these figures, obtained by different analysts, agree very nearly as well as those obtained by the previous method, with one exception. The general tendency, however, seems to be in the direction of obtaining slightly lower figures by this method than by Method I. This is doubtless due to the fact that the free arsenious oxid present in the Paris green does not go into solution with the dilute hydrochloric acid used. The referee has observed many times that quite long stirring is necessary to cause the free arsenious oxid to go into solution when pure samples of Paris green are used, and that it is practically impossible to get the free arsenious oxid in solution when samples containing large amounts of free arsenious oxid are used. In this connection it will be noticed that the experience of other analysts has been the same as that of the referee and that Mr. Thatcher gives figures to prove the truth of this statement. I would also add that, as Mr. Beans says, the method can be shortened by standardizing the iodin directly against chemically pure arsenious oxid that has been dissolved in sodium bicarbonate. This, unlike sodium hydroxid, does not seem to cause the arsenites to be oxidized to arsenates in boiling solution.

Neither of the methods for soluble arsenious oxid give very accurate results. In Method I, which is supposed to show the free arsenious oxid existing as such in the green, excluding the extremely high figures 1.67 and 1.63, the results vary from an average of 0.40 per cent to an average of 0.98 per cent. While this showing would be very poor in most determinations, it is not so unsatisfactory in this particular case as it is only to gain an approximate idea of the amount of the arsenious oxid existing as such in the Paris green that this determination is made. In fact, we do not at the present time know within half a per cent how much free arsenious oxid

different plants can stand. Method II, leaving out the extremely high figure 3.87, gives results that vary from an average of 2.07 per cent to an average of 3.63 per cent. The figures obtained by this method seem to the referee to give some idea of the stability of the green, and hence this determination is a rough measure of the action of the insecticide in actual orchard practice. Looking at the matter in this light, it is seen that if the results by Method I are low, and by Method II high, the green is unstable and consequently unfit for use, while if the results by both these methods are high, then free arsenious oxid is present as such in the green, thus again rendering it unfit for use. The only way that results of a comparative nature can be obtained by Method II is to follow extremely strict rules as to the amount of water to be used, the length of time of extraction, and the number of times per day that the mixture of green and water is to be shaken.

The figures for soluble copper oxid have no special significance, but the determination was made in the hopes that someone would, during the year, work out (if such a thing is possible) the relation between the green broken up, and the soluble copper oxid that goes into solution.

The averages of the results obtained by different chemists following Method I for total copper oxid agree fairly well with each other. Only one chemist seemed to experience any difficulty in carrying out this method. Your referee is of the opinion from his own experience with this method that the results obtained by it are slightly below the truth, and that one must be very careful not to make the copper solution too acid with acetic acid, or extremely varying results will be obtained.

As to Method II for total copper oxid, here again most of the averages agree well with each other, but are not as close together as one would desire. In most cases individual chemists seem to obtain slightly higher results by this method than by Method I.

London Purple.

Table III.—*Results of work done with London purple.*

Analyst.	H_2O.	Total As_2O_3.	Total As_2O_5.	Soluble As_2O_3.	Soluble As_2O_5.
	Per ct.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
L. H. Smith, Illinois	4.10	16.85	25.35	10.83	4.58
	4.18	16.63	27.90	.....	.....
	.....	16.56	26.19	10.60	4.73
	.....	16.41	27.06	.....	.....
H. T. Beans, Idaho	4.06	16.60	28.33	10.42	4.08
	4.07	16.54	27.82	10.51	3.54
	.....	15.58	.....	.....	.....
T. M. Price, Maryland	3.80	16.50	27.18	10.75	4.25
R. W. Thatcher, Washington	3.64	16.56	27.16	10.63	4.01
	3.63	16.66	27.20	10.68	4.21
D. L. Cleaves, Massachusetts (Hatch)	4.55	16.65	.....	.....	.....
	4.34	16.69	.....	.....	.....
R. J. Davidson, Virginia	4.07	16.84	25.71	10.83	5.36
	4.08	16.79	25.20	10.79	5.42
	.....	16.72	25.52	10.57	5.84
	.....	16.79	25.20	10.62	.....
H. J. Warner, Bureau of Chemistry, U. S. Department of Agriculture.	3.90	16.87	27.36	11.15	3.94
	3.74	16.87	27.19	11.15	3.80
James Emery, Biochemic Division, Bureau of Animal Industry, U. S. Department of Agriculture.	.....	16.65	27.45	.....	.....
	.....	16.72	.....	.....	.....
J. K. Haywood, Bureau of Chemistry, U. S. Department of Agriculture.	3.90	16.64	27.02	11.02	4.00
	3.90	16.78	27.10	11.04	4.20

COMMENTS OF ANALYSTS.

L. H. Smith.—The method for determining total arsenic acid was not satisfactory owing to the dark-colored solution.

R. W. Thatcher.—After repeated trials I was finally able to obtain fairly concordant results in determinations of total arsenic acid. I regard the method as very unsatisfactory, as it is only with great difficulty that the addition of too much thiosulphate is avoided.

In the determination of soluble arsenious and arsenic acids I tried the effect of suspending 1 gram of substance in 1,000 cc of water, with the following results: Soluble As_2O_3=12.19, 12.36 and soluble As_2O_5=6.81, 6.66.

D. L. Cleaves.—It was found impossible to determine the total arsenic oxid, as a satisfactory end point could not be obtained.

DISCUSSION OF RESULTS.

The results obtained by different chemists upon the method for determining total arsenious oxid in London purple leaves little to be desired, and at least show that close results can be obtained by different analysts who employ this method.

The results obtained by using the method for total arsenic oxid, while they vary a good deal, show that this method is worthy of further study. Five analysts obtained results that agree very closely with each other; one obtained results slightly below the general average; one obtained results slightly above the general average; one obtained figures which, separately, were unsatisfactory, but whose average agreed with the figures of the other five, and one was not able to obtain satisfactory results at all. Your referee, who first applied this method to the analysis of London purple, is aware of the fact that the end points are very hard to read, especially for one who has had no experience with the method. He is, however, of the opinion that as one gets more familiar with this method its difficult features disappear, and that one can finally arrive at such a point that identical results, or very closely agreeing results, will be obtained every time.

The results obtained by the method for determining soluble arsenious oxid in London purple agree fairly well. The results obtained by the method for soluble arsenic oxid vary to quite an extent, but with one exception are not widely different from one another.

Copper Carbonate.

TABLE IV.—*Results of work done on copper carbonate.*

Analyst.	Copper oxid.		
	Method I.	Method II.	Method by electrolysis.
	Per cent.	*Per cent.*	*Per cent.*
R. J. Davidson, Virginia	58.47	58.23	.....
	58.46	58.53	.....
	.....	58.29	.....
H. J. Warner, Bureau of Chemistry, U. S. Department of Agriculture	58.42	58.53	.....
	.....	58.96	.....
James Emery, Biochemic Division, Bureau of Animal Industry, U. S. Department of Agriculture	58.54	58.96	58.47
	58.54	58.96	58.60
	58.14	58.96	.....
J. K. Haywood, Bureau of Chemistry, U. S. Department of Agriculture	58.24	59.01	.....
	58.24	59.01	.....

The results obtained by Method I agree with one another much better than they did when this method was applied to Paris green, and seem to leave very little to be desired. Mr. Emery, the associate referee, made electrolytic determinations of the copper in this compound which showed that Method I for such compounds as these gives extremely accurate results. Method II gives results which in three out of the four cases are slightly too high.

Potassium Cyanid.

Table V.—*Results of work done on potassium cyanid.*

Analyst.	Potassium cyanid.
	Per cent.
R. J. Davidson, Virginia	52.42
	52.42
	52.42
H. J. Warner, Bureau of Chemistry, U. S. Department of Agriculture	52.75
	52.75
James Emery, Biochemic Division, Bureau of Animal Industry, U. S. Department of Agriculture	52.31
	52.31
J. K. Haywood, Bureau of Chemistry, U. S. Department of Agriculture	52.87
	52.87
	53.12

The results obtained by using the method as outlined for the determination of cyanogen and then calculating the results to potassium cyanid are very good and agree exceedingly well with one another, especially when we take into consideration the fact that it was very difficult to obtain even samples in the beginning, on account of the hygroscopic nature of the substance employed.

Soda Lye.

Table VI.—*Results of work done on soda lye.*

Analyst.	Sodium hydrate.		Sodium carbonate.	
	Method I.	Method II.[a]	Method I.	Method II.[a]
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
R. J. Davidson, Virginia	73.12	72.22	3.61	5.28
	73.12	.....	3.61	.....
H. J. Warner, Bureau of Chemistry, U. S. Department of Agriculture	72.16	70.58	2.29	3.35
	72.16	70.44	2.29	3.35
James Emery, Biochemic Division, Bureau of Animal Industry, U. S. Department of Agriculture	71.60	71.51	4.85	4.36
	71.60	.....	4.63	.....
	71.62	.....	4.63	.....
J. K. Haywood, Bureau of Chemistry, U. S. Department of Agriculture	71.84	70.96	2.37	3.17
	71.84	70.80	2.13	3.17
	.....	.....	.....	3.17

[a] Third normal potassium acid sulphate was used for the titration.

It was exceedingly difficult to prepare the various samples of soda lye so that they would be strictly comparable with one another. Large pieces of the lye were broken up, and these smaller pieces were placed in bottles whose stoppers were covered with paraffin so that the contents would not absorb moisture. Working, however,

with as great rapidity as possible, it was not possible to avoid having some samples absorb slightly more moisture and carbon dioxid than others. Taking, then, these facts into consideration, quite good results were obtained upon these samples for sodium hydroxid by both Methods I and II. The results obtained for sodium carbonate are not so good, but very likely this is largely due to the fact that the samples absorbed different amounts of carbon dioxid, and that the analysts failed to use water that was entirely carbon-dioxid-free.

Upon considering each analyst's work, it will be seen that by Method I higher results are obtained for sodium hydroxid than by Method II, while by Method I lower results are obtained for sodium carbonate than by Method II, with the exception of Mr. Emery's figures.

It is the opinion of the referee that the results obtained by Method II are more accurate than the results obtained by Method I, for the following reasons: In Method I, after the carbonates are precipitated out by barium chlorid, the supernatant liquid is titrated for the sodium hydroxid present. Since barium carbonate is soluble to quite an extent in water, that portion which is soluble is also titrated as sodium hydroxid, thus increasing the sodium hydroxid figure. In Method II all of the sodium hydroxid and one-half the sodium carbonate is first titrated, then the other half of the sodium carbonate, so there does not seem to be the same chance for error.

Whale-Oil Soap.

Table VII.—*Results of work done on whale-oil soap.*

Analyst.	Moisture.
	Per cent.
James Emery, Biochemic Division, Bureau of Animal Industry, U. S. Department of Agriculture	37.41
J. K. Haywood, Bureau of Chemistry, U. S. Department of Agriculture	37.47
	37.37

The complete work upon soap samples was not undertaken by any of the chemists engaged in the work, but two of them made determinations of the moisture. As will be seen, their results agree very well with each other.

Formalin.

Table VIII.—*Results of work done on formalin.*

Analyst.	Formaldehyde.				
	Method I.	Method II, by weighing.	Method II, by distillation.	Method III.	Iodometric method.[a]
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
R. W. Thatcher, Washington	36.56	.....	36.91	35.31	36.91
	36.58	.....	37.06	34.91	36.58
	36.76	.....	.....	35.03	36.69
E. F. Ladd, North Dakota	.....	.....	.....	35.53	.....
	.....	.....	.....	35.53	.....
	.....	.....	.....	35.45	.....
James Emery, Biochemic Division, Bureau of Animal Industry, U. S. Department of Agriculture.	37.95	.....	.....	.....	.....
	38.00	.....	.....	.....	.....
J. K. Haywood, Bureau of Chemistry, U. S. Department of Agriculture.	37.18	36.50	.....	36.20	.....
	37.12	36.16	.....	36.85	.....

[a] Taken from Allen's Com. Org. Analysis, vol. 1, p. 229.

COMMENTS BY ANALYSTS.

R. W. Thatcher.—In Method II, I attempted to dry and weigh the hexa-methyl-tetramine formed by evaporating at 80° C. until the mixture began to sputter and then placing in a vacuum desiccator over sulphuric acid, but found that a month's drying in this manner had not removed half the remaining moisture, hence I abandoned this method as impracticable. I also made three determinations on this sample by the iodometric method.

E. F. Ladd.—Method I gave very unsatisfactory results. We tried the best grades of hydrogen-peroxid that could be found in the market, but could not secure concordant results. Ours ranged from 22 per cent to about 33 per cent. Method II proved wholly unsatisfactory in our hands, as both of these methods have with us in the past.

J. K. Haywood.—In Method II the dishes containing the hexa-methyl-tetramine continued to lose weight for three weeks, and were still losing weight when the determination was stopped. At the end of almost two weeks the loss each day was practically constant, and at this time the weight of the residue in the dishes showed the presence of 36.66 and 36.45 per cent formaldehyde. After about three more days the weight had decreased to such an extent as to make the figures for formaldehyde 36.50 and 36.16 per cent. It was very hard to read the end point in Method III.

SUGGESTIONS.

From the above work done upon formalin and the comments made by the various chemists engaged in the work, your referee is of the opinion that Method II (by weighing the residue) is nearly valueless and should be abandoned. It also hardly appears best to do further work upon Method III. It appears, then, that the two most promising methods are I and II (by distilling off the excess of ammonia). It might also be well to test the iodometric method referred to by Mr. Thatcher, and the cyanid method referred to by Mr. Houston last year.

TOBACCO EXTRACT.

TABLE IX.—*Results of work done on tobacco extract.*

Analyst.	Nicotine.		
	Method I.	Method II.	Method III.
	Per cent.	*Per cent.*	*Per cent.*
R. J. Davidson, Va	3 distillations.. 26.20	After 24 hours standing..... 34.88	Ran as directed 14.71
	4 distillations.. 26.40		Extra extraction..... 15.18
	4 distillations.. 26.40	After 72 hours standing at 40° C..... 26.61	Extra extraction..... 21.00
	5 distillations.. 26.49		Extra extraction..... 16.65
			Extra extraction..... 23.67
		After 72 hours standing at 40° C..... 28.40	
		After 48 hours standing and heating to 40° C. for 72 hours 26.40	
James Emery, Biochemic Division, Bureau of Animal Industry, U. S. Department of Agriculture.	Repeated distillation and small amount of substance taken..... 27.83	After 36 hours standing in breakers..... 25.65	Ran as directed 17.64
		25.75	18.14
		26.87	Extra extraction 21.41
			21.30
J. K. Haywood, Bureau of Chemistry, U. S. Department of Agriculture.	28.04	After 36 hours standing..... 28.45	Ran as directed 19.92
	25.73		18.24
	25.79		Extra extraction 23.42
	26.52		24.18

COMMENTS BY ANALYSTS.

R. J. Davidson.—By running Method II exactly as directed, ammonia was still present, so large results were obtained. By allowing the vessel to stand seventy-two hours at 40° C., ammonia was absent and good results were obtained. A duplicate of this gave high results. One that stood forty-eight hours and then seventy-two hours at 40° C. gave good results.

By Method III, when this was run exactly as described, very low results were obtained; when it was extracted with 12, 10, 10, 10 and 10 cc, 15.18 per cent was obtained; when it was extracted with 12, 11, 10, and 98 cc, 16.65 per cent was obtained, and when it was extracted with 12, 11, 10, and 98 cc, and then with 12, 11, and 10 cc, 23.67 per cent was obtained.

James Emery.—Instead of following directions exactly for Method I, a smaller amount of the extract was weighed out than is directed in the method. The distillation was continued until only a small amount remained in the distillation flask, then the distillating flask was refilled with water and again distilled with steam. For Method II, the extract was weighed out in beakers instead of flasks to allow the ammonia to escape and allowed to stand with the concentrated sodium hydroxid for thirty-six hours. When Method III was run as directed, low results were obtained, but where the magma was extracted three additional times, with 50 cc each time, results of 21.41 per cent and 21.30 per cent were obtained. No more could be extracted.

J. K. Haywood.—After standing with sodium hydroxid for thirty-six hours, Method II gave the result submitted, but a very slight smell of ammonia seemed to be present. When Method III was run as directed, very low results were obtained. The magma was extracted twelve extra times with 10-cc portions of petroleum-ether, and the results 23.42 per cent and 24.8 per cent as given were obtained.

The sample of extract sent out this year was extremely difficult to work upon, since it contained a very great excess of ammonia and ammonium salts. It is not often that one would be called upon to analyze a sample that presented the difficulties which this one did.

Your referee is of the opinion that if Method I is properly carried out, fair results may be obtained, and thinks that good results may also be obtained by Method II if one adopts the scheme devised by Mr. Emery, of weighing the extract out in beakers and allowing it to stand in these in contact with concentrated sodium hydroxid for about forty-eight hours. Method III evidently gives low results, as has been shown in these experiments and in work done by one of our former referees.

In conclusion, I desire to express my thanks to those who have so kindly cooperated with me in this work. Especially my thanks are due to Mr. Emery, the associate referee.

Mr. F. W. Traphagen, of the Montana Experiment Station, sent in figures upon various of these groups but unfortunately they were received too late to be incorporated in the report.

RECOMMENDATIONS.

I would respectfully recommend:

(1) That, as Method I, for total arsenious oxid in Paris green has been thoroughly tested and shown to give good results, and as your referee has thoroughly tested this method, compared it with other methods, and always found that it gave most excellent results, it be adopted as one of the official methods of the A. O. A. C.

(2) That Method II for total arsenious oxid in Paris green be tested next year upon samples of Paris green that contain a large amount of free arsenious oxid.

(3) That both methods for soluble arsenious oxid in Paris green be further tested,

and that the referee try to so modify the directions that more concordant results may be obtained.

(4) That Methods I and II for copper oxid in Paris green be further tested and compared with an electrolytic determination of the copper oxid.

(5) That all methods of analysis of London purple be further tested.

(6) That Methods I and II for determining copper oxid in copper carbonate be compared with the electrolytic method.

(7) That the cyanid method be tested upon samples of known strength or compared with some well-known gravimetric method.

(8) That both the methods of analysis of soda lyes be further tested, using lyes which contain a larger percentage of sodium carbonate.

(9) That the methods of analysis of soaps be further tested.

(10) That Method II for formalin (by weighing the residue) and Method III be dropped and that Methods I and II (by distillation) be further tested and compared with the cyanid and iodometric methods.

(11) That Methods I and II for nicotin be further tested upon extracts containing both large and small amounts of nicotin, and that Method III be dropped for determining large amounts of nicotin, but tested upon extracts containing small amounts of nicotin.

The PRESIDENT: Discussion is now in order.

Mr. DAVIDSON. In regard to the iodin solution, I would like to ask the referee if it would be possible to make it half strength. It makes a considerable difference in the percentage by weakening the solution just a little.

Mr. HAYWOOD. In connection with that I will say that I think it might be a very good idea to make the iodin solution weaker than it is. I have noticed, myself, that 0.2 cc in the burette reading makes a great difference in the percentage, and anyone is apt to make an error of 0.1 to 0.2 cc in this reading.

Mr. DAVIDSON. In regard to the nicotin determinations in tobacco extracts, I would state that this sample was very rich in ammonia, and I, like Mr. Emery, used a beaker in which to treat the extract with sodium hydrate instead of a flask. I think this is absolutely necessary because of the large amount of ammonia present.

Mr. HAYWOOD. It is undoubtedly shown by all of our work that the expulsions of ammonia by sodium hydrate must be effected in an open vessel. I believe that when Mr. Winton originally got out this method he worked upon extracts that did not contain such large amounts of the ammonia and ammonium salts as the sample sent out by us, and therefore his method will have to be modified to some extent to give good results with such extracts as the one worked upon. As Mr. Winton, the originator of this method, is here, I would like to ask him if he worked upon samples containing large amounts of free ammonia.

Mr. WINTON. I do not remember about the ammonia, but I do remember that the process did not seem to give as sharp an end point as the old Kissling method. I devoted my attention more to that point than to the study of the effect of varying quantities of ammonia upon the determination.

Mr. Haywood. In connection with this study on insecticides, I desire to call attention to some work that we are now carrying on in collaboration with the Division of Entomology on the effect of varying amounts of soluble arsenic upon the foliage of different kinds of trees. We found in working with Paris green that there are three conditions that may give rise to the scorching of the foliage by the soluble arsenic present in the green: First, the arsenious oxid which exists as such in the Paris green is injurious and scorches the foliage; second, there are certain greens which are badly made and which in consequence are soon broken up by the moisture and carbon dioxid in the air, thus releasing free arsenious oxid; third, if the green is very fine it is more easily broken up by water, and consequently free arsenious oxid is set free, which injures the foliage. Our preliminary work upon this subject indicates that apple and pear trees can stand Paris green containing from 7 to 8 per cent of free arsenious oxid, while peach trees can stand Paris green containing about 4 per cent. I will say also in this connection that all the determinations of arsenious oxid were made by the ten-day extraction method and are consequently much higher than the results would have been by using a twenty-four-hour extraction, as was done by many chemists in past years.

Mr. Davidson. I do not know whether it is necessary to make a motion, but if it is I would like to make one as follows: That the referee for next year be instructed to try the effect of changing the strength of the iodin solution in the determination of total arsenic in Paris green.

Mr. Haywood. I second the motion.

The motion was adopted.

Mr. Davidson. In connection with the nicotin determination, I would also like to make a motion that this point we have just spoken of, concerning the desirability of allowing the extract to stand in beakers instead of flasks, be called to the attention of the referee for next year.

Mr. Haywood. I second the motion.

The motion prevailed.

Mr. Winton. With reference to the question of large amounts of ammonia in nicotin extracts, I will say that I have had success in removing this ammonia by placing the dish containing the extract under a bell jar with a dish containing strong sulphuric acid and drawing a current of air over the dishes.

Mr. Haywood. I have tried the method suggested by Mr. Winton and have found that it works quite satisfactorily. I think the Winton method as well as the Lloyd method will have to be modified to quite an extent in order that they give good results upon substances containing such a large amount of nicotin. They were both evidently originally devised for extracts which contain only small amounts of

nicotin and little ammonia. It would very likely be best not to make any cast-iron rules for the chemists to follow. In the Winton method, for example, it might be directed that the extract be allowed to stand in contact with sodium hydrate until all ammonia is removed, and in the Lloyd method that the extractions with ether be continued until all nicotin is extracted from the magma.

Mr. WILEY. There is a point that I would like to make right here in connection with this discussion. It seems to me that the time has passed when we must give minute details and directions to analysts as to how they are to carry on the work. It would be much better to give a broad outline of the plan and let each analyst work out the details for himself. When this association first began its work minute details as to manipulation were undoubtedly necessary, but our men have now been educated up to the point where they are expert analysts and will no doubt obtain better results by being allowed to work out the details for themselves. In other words, it is not the work of the analyst that we wish to test, but the working of the method.

The PRESIDENT. If there is no objection, the report of the chairman of the committee on fertilizer legislation will be called for at this time.

Mr. WILEY. The only report that I have to make on this subject is the one that the president of the association has prepared.

REPORT OF COMMITTEE ON FERTILIZER LEGISLATION.

By H. J. WHEELER.

As chairman of the committee on uniform fertilizer legislation of the Association of American Agricultural Colleges and Experiment Stations I will say that the matter of fertilizer legislation was brought up at the instance of our committee before the United States Commission on Uniform Legislation at its last meeting and the members from the respective States were instructed by a resolution to that effect to assist in so far as they could in securing uniformity of legislation along the lines laid down by this association and the Association of American Agricultural Colleges and Experiment Stations. As chairman of the committee for the latter association I have been consulted by several States in regard to fertilizer laws. Something is being done continually to bring about uniformity in legislation in regard to fertilizers.

Mr. WILEY. I move that the report be accepted and the committee continued.

The motion was adopted.

The PRESIDENT. Are there any business matters to come before us at this time?

Mr. WILEY. I would like to make one or two announcements. The agent of the Trunk Line is here to validate tickets. The tickets of those who came over the southeastern line he has taken down to the Southern Railway office.

I will state that the chiefs of the laboratories of the Bureau of Chemistry are present and will be glad to receive members of this association and to show them through our laboratories after the adjournment of this meeting.

The PRESIDENT. The association will bear in mind that in regard to the recommendations of referees matters of minor importance and matters that are urgent may be acted upon at this time by a two-thirds vote. I will ask the chairman of Committee A on recommendations if there are any such matters to be considered.

Mr. STREET. I think that the majority of the recommendations made to us fall within this scope. We are ready to report on all of our sections except insecticides.

REPORT OF COMMITTEE A ON RECOMMENDATIONS.

SOILS.

Mr. STREET. It is recommended—

That the N/200 hydrochloric acid method be given further trial.

That samples be so taken that it will be possible to determine the available potash and phosphoric acid in each stratum sampled to a total depth of 3 or 4 feet.

That the methods for the analysis of alkali soils be referred to the referee, with instructions to determine the most desirable amount of soil and the amount of water to be used in dissolving the soluble salts.

That in the selection of soils for examination, virgin soils be given a place among the soils worked upon.

That the quantitative method for the determination of the acidity of soils be made a provisional method.[a]

Mr. VAN SLYKE. I move that the recommendations be adopted as read.

Mr. HOPKINS. I notice that the recommendations include an arbitrary division as to the depth of the different strata to be taken in determining available phosphoric acid. The provisional method for soil sampling which was adopted last year states that we shall sample distinctly different strata, rather than make an arbitrary division. You are all aware that we frequently find soils that extend to the depth of 11 to 17 inches. The character of the soil changes very much, and it seems to me that it might be well to modify the provisional method for soil sampling, if the recommendation could be modified to include the provisional method.

Mr. STREET. I think that is the idea of the recommendation. We would be willing to incorporate that.

Mr. HOPKINS. I make a motion to so amend the provisional method relating to the sampling of soils. I would like to ask also that the method for determining the acidity of soils be adopted as a provisional method, and that it be referred to the referee for investigation next year. A number of members have spoken to me regarding the details of the method. I am sure a considerable amount of work will be done in this line, and, as we have no method in the association for such determinations, I think perhaps it would be well if this could be adopted as a provisional method and further investigation encouraged next year. I will move to further amend the report to that effect.

---

[a] As amended.

The motion prevailed, and the original motion, as amended, was then adopted.

POTASH.

Mr. STREET. It is recommended—

That further experiments be conducted for the purpose of securing a method that will dissolve all of the potash in mixed fertilizers, giving attention to the amount of material used and the amount of water used for making the solution.

That the referee, if he have sufficient time, study methods for the determination of moisture in potash salts.

Mr. VAN SLYKE. I move that the recommendations, as read, be adopted.

This was carried.

ASH.

Mr. STREET. It is recommended—

That the referee be requested to make a further study of the fusion method for the determination of sulphur, and also methods to determine how much of the sulphur belongs to the ash.[a]

That the method of determining chlorin by ignition with sodium carbonate be adopted as a provisional method.

Mr. WILEY. It seems to me that there is a very important point under ash which the committee ought to consider. I do not know that I am prepared to amend the report in any way, but the question of determining the sulphur in the ash of a plant ought to be considered. All these fusion methods have for their object the determination of total sulphur in the form of sulphuric acid. I know that almost all the sulphur that exists in the plant is not properly found in the ash, but I think the referee on ash ought to work on a method to determine how much of the sulphur does belong to the ash. So I would like to suggest, and if it meets with the approval of the association it would be advisable to make a motion, that the referee be instructed to investigate methods by which we can determine how much of the sulphur in plants and plant products belongs to the ash. Of course the remainder belongs to the organic compound. I move that the report of the committee be amended to this extent, that the referee be instructed to investigate the method of determining what part of the sulphur in plants and plant products should be considered in the ash.

The amendment was carried, and the report on ash was adopted as amended.

NITROGEN.

Mr. STREET. Under nitrogen there are two recommendations—

That the subject of the availability of organic nitrogen be further studied with the view to so perfecting the neutral and alkaline permanganate methods as to secure concordant results.

That it be earnestly urged that, in reporting the analyses of complete fertilizers, the amounts of nitrogen existing in the form of nitrates, ammonia salts, and organic nitrogen be specifically stated.

---

[a] As amended.

On motion, the recommendations on nitrogen were adopted.

Mr. STREET. Our only report on phosphoric acid is that the committee desires to get the sense of the association as to the advisability of discontinuing the investigations on basic slag. From the representation of the committee, made from our experience, it seems that the use of basic slag is extremely limited. It was suggested that the association should not work on the matter, as the slag is so little used.

The PRESIDENT. Does the association desire to take any action in this matter?

Mr. HOPKINS. I would say that a firm in Philadelphia is buying considerable basic slag which it is putting out. It seems that the use of this material is on the increase.

GENERAL RECOMMENDATION.

Mr. STREET. We have one general recommendation, which was considered by the referees, which reads as follows:

In the comparison of methods, in addition to the general letter requesting cooperation, it is recommended that the referee invite the assistance of workers experienced in the special portions of the work assigned to him.

This recommendation was adopted.

[NOTE BY THE EDITOR.—The following recommendations were approved by Committee A, after the adjournment of the meeting, and forwarded by the chairman with the following comment:]

DECEMBER 13, 1902.

DEAR SIR: In reply to your letter of December 11, I inclose herewith the balance of the report of Committee A on recommendations, covering the recommendations of the referee on insecticides. You will notice that the first recommendation alone entails any change in methods, and the committee in this case has accepted the long experience of Mr. Haywood in this kind of work as strong evidence that the change is a worthy one. The other recommendations refer merely to details or suggestions to the new referee.

Very respectfully, JOHN PHILLIPS STREET, *Chairman.*

INSECTICIDES.

(1) That, as Method I, for total arsenious oxid in Paris green has been thoroughly tested and shown to give good results, and, as your referee has thoroughly tested this method, compared it with other methods, and has always found that it gave most excellent results, it be adopted as one of the official methods of the A. O. A. C.

(2) That Method II for total arsenious oxid in Paris green be tested next year upon samples of Paris green that contain a large amount of free arsenious oxid.

(3) That both methods for soluble arsenious oxid in Paris green be further tested and that the referee try to so modify the directions that more concordant results may be obtained.

(4) That Methods I and II for copper oxid in Paris green be further tested and compared with an electrolytic determination of the copper oxid.

(5) That all of the methods of analysis of London purple be further tested.

(6) That Methods I and II for determining copper oxid in copper carbonate be compared with the electrolytic method.

(7) That the cyanide method be tested upon samples of known strength or compared with some well-known gravimetric method.

(8) That both the methods of analysis of soda lyes be further tested, using lyes which contain a larger percentage of sodium carbonate.

(9) That the methods of analysis of soaps be further tested.

(10) That Method II for formalin (by weighing the residue) and Method III be dropped, and that Methods I and II (by distillation) be further tested and compared with the cyanid and iodimetric methods.

(11) That Methods I and II for nicotin be further tested upon extracts containing both large and small amounts of nicotin and that Method III be dropped for determining large amounts of nicotin, but tested upon extracts containing small amounts of nicotin.

JOHN PHILLIPS STREET.
M. E. JAFFA.
B. B. ROSS.
E. G. RUNYAN.
F. P. VEITCH.

The PRESIDENT. I will call on the chairman of Committee B on recommendations for his report.

REPORT OF COMMITTEE B ON RECOMMENDATIONS.

Mr. KRUG. With reference to dairy products, there are no changes in the method. The committee would, however, recommend that the referee for next year make a study of the effects of preservatives on the albumin of milk.

Mr. WILEY. I would like to ask a question. Does that mean the albumin proper or all of the protein of the milk. I infer that it means all of the protein.

Mr. KRUG. If the referee on dairy products were here, he could inform you. I am not familiar with the subject.

The recommendation was adopted as read.

FEEDING STUFFS.

Mr. KRUG. With reference to feeding stuffs the committee recommends that from the sixteenth line,[a] the method be changed to read as follows, following the directions prescribed by Kröber:

The solution is made up to 400 cc with 12 per cent hydrochloric acid, and allowed to stand overnight. The amorphous black precipitate is filtered into a tared gooch through an asbestos felt, washed carefully with 150 cc of water in such a way that the water is not entirely removed from the crucible until the very last, then dried to constant weight by heating four hours at 100° C., cooled, and weighed in a weighing bottle, the increase in weight being reckoned as phloroglucid. To calculate the furfurol from the phloroglucid, use the following formulæ:

For weight of phloroglucid (a) under 0.03 grams.

$$\text{Furfurol} = (a + 0.0052) \times 0.5170.$$
$$\text{Pentoses} = (a + 0.0052) \times 1.0170.$$
$$\text{Pentosans} = (a + 0.0052) \times 0.8949.$$

For weights of phloroglucid (a) from 0.03 grams to 0.300 grams Kröber's table is recommended.[b] If this is not available, use the formulæ:

$$\text{Furfurol} = (a + 0.0052) \times 0.5185.$$
$$\text{Pentoses} = (a + 0.0052) \times 1.0075.$$
$$\text{Pentosans} = (a + 0.0052) \times 0.8866.$$

For weights of phloroglucid (a) over 0.300 grams.

$$\text{Furfurol} = (a + 0.0052) \times 0.5180.$$
$$\text{Pentoses} = (a + 0.0052) \times 1.0026.$$
$$\text{Pentosans} = (a + 0.0052) \times 0.8824.$$

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[a] Circular 7, Div. of Chem., U. S. Dept. Agr. Provisional method for the determinations of pentosans by means of phloroglucol.

[b] Journal für Landwirtschaft 48: 1900, p. 379.

Mr. KRUG. I think it would be advisable to make these changes at this time.

Mr. WILEY. Does this involve a change in the method?

The PRESIDENT. The Chair understands that this is a change of vital importance at this time. Is there anything to be said upon the adoption of this?

Mr. BROWNE. Is this a provisional method or an official method?

Mr. KRUG. This is a provisional method.

On motion the recommendation was adopted.

Mr. KRUG (continuing report). The next recommendation in connection with this same method is the adoption of Kröber's factors.

Mr. WILEY. How much do they differ from the old factors?

Mr. BROWNE. Very little. I think we ought to adopt these factors.

On motion of Mr. Krug, the recommendation was adopted.

TANNIN.

Mr. KRUG (continuing report). I understand that we have here changes in the official method on tannin[a] that must go over until next year. I would like to read them to the association if there is no objection.

To omit the moisture determinations in extracts.

To change (*b*) in paragraph III so as to read:

Evaporations shall take place under precisely the same conditions as to contact with steam or with a metallic plate; all dryings called for after evaporation shall be done by one of the following methods under precisely the same conditions, so that the different residues of each analysis may occupy the same shelves in the drying oven.

1. For eight hours at the temperature of boiling water in steam oven.
2. For six hours at 100° C. in air bath.
3. For five hours at 100° C. in vacuo.

V. Soluble solids to read as follows:

Single pleated filter paper (S and S No. 590, 15 cm) shall be used. To 2 grams kaolin add 75 cc of the tanning solution, stir, let stand fifteen minutes and decant as much as possible (not on the filter), add 75 cc of the solution, stir, and pour on the filter. Keep filter full, reject the first 150 cc of filtrate, evaporate, and dry next 100 cc. The portion dried for determination shall be perfectly clear and evaporation during filtration must be guarded against.

VI. Non-tannins: Two grams kaolin to be used when filtering.

Omit paragraph VIII on testing hide powder and section (*b*) of paragraph IX, on testing nontannin filtrate for soluble hide.

The following provisional method for the determination of total acidity in liquors is recommended:

Place 100 cc of the liquor in a 500-cc flask and make up to the mark with water. To 100 cc of diluted liquor in a flask with tube condenser add 2 grams of chemically pure animal charcoal. Heat to boiling temperature with frequent shaking, cool, filter, and titrate an aliquot portion with decinormal alkali.

The following suggestions are made by the referee on tannin with reference to next year's work:

Additional experimental work on soluble solids, acid determinations, and on the amount of extract taken for analysis.

A comparative study with the following modifications of the charcoal method is recommended: To 100 cc of diluted liquor, prepared as in the provisional method, add 2.5 grams chemically pure animal charcoal, stir every fifteen minutes for two hours, filter, and titrate an aliquot portion with decinormal alkali.

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[a] Subsequent investigation showed that this method had never been adopted as official, and therefore these changes in a provisional method became effective for the work of 1902–1903.

The referee also recommends that the work during the next year shall include a study of the correction method for the tannin absorption of the filter paper which was adopted at the last meeting of the International Association of Leather Trades Chemists, held at Leeds, England.

The PRESIDENT. Is it the desire of the association that action be taken?

Mr. KRUG. I think it would be well to have these recommendations held over.[a]

If permissible at this time, I would like to say that the report of the European Leather Trades Chemists Association, to which I referred yesterday, was received this morning, and I make a motion that the secretary be authorized to incorporate an extract of the report in the proceedings of this association.

[NOTE BY THE EDITOR.—The following extract from this report is inserted in accordance with the above instructions:]

At the last convention of the International Association of Leather Trades Chemists the following resolutions, which embody the changes made in the international method, were adopted:

(A) The filtration of the solution for analysis may take place through any paper which may be considered more suitable for the particular case, and with or without the use of kaolin, the absorption of the tanning matter being corrected for by an amount determined by a similar filtration of a clear solution. Perfectly clear solutions need not be filtered.

Following the discussion on the filter paper in tanning analysis the following resolution was carried:

(B) To determine the correction, about 500 cc of the tanning solution of the strength prescribed for analysis is obtained perfectly clear, preferably by the method of filtration, which is to be corrected for. After thorough mixing, 50 cc is evaporated to determine "total soluble No. 1." A portion of the remainder is then filtered in the manner for which correction is to be made, and 50 cc of the filtrate is evaporated for "total soluble No. 2." Deducting No. 2 from No. 1 the difference is the correction required, which must be added to the "total soluble" found by analysis. It is generally advisable, both in analysis and in the second filtration for correction, to filter first 150 cc, which in analysis may be used for determination of nontannins, and then to employ the next 50 cc for evaporation, keeping the filter full during the operation; but whatever procedure is adopted must be rigidly adhered to in all analyses to which the correction is applied. Where kaolin is employed a constant weighted quantity (1 or 2 grams) must be used, which is first washed with 75 cc of the liquor by decantation, and then washed onto the filter with a further quantity of liquor, of which 200 cc is filtered as above.

(C) In making samples of spent tans in cases where the prescribed strength can not otherwise be obtained, it is permissible to concentrate the whole solution. It is advisable, where ready means exist, to concentrate in vacuo, failing the necessary apparatus, concentration may be carried out by evaporation in a flask, in the neck of which a funnel is placed to prevent oxidation.

(D) That the filter method of determination of nontannins, as prescribed in the rules of the association, remain the official method until the next conference, but that members be permitted to employ the chrome hide-powder method of the conference of the American Association of Official Agricultural Chemists in 1901 where it is desired, the fact being clearly stated on the report that the A. O. A. C. method has been employed, and not that of the I. A. L. T. C.

(E) Used liquors must be analyzed by the A. O. A. C. method of 1901.

The PRESIDENT. If there is no further report from Committee B, the Chair will call for the report of Committee C on recommendations.

[a] As a circular letter addressed to the executive committee procured permission to insert the word "provisional" over methods on tannin in Bulletin 46, the changes above noted have been considered by the referee as a part of the provisional methods.

REPORT OF COMMITTEE C ON RECOMMENDATIONS.

FOOD ADULTERATION.

Mr. LEACH. The committee has only one recommendation to make, namely, that the association empower the referee on food adulteration to assign the work as he may see fit, acting on the advice of the executive committee. In this work the number of subjects is greatly in excess of the number of men who can work upon them, and it is desired to further subdivide the work of the coming year. It is not possible at present to definitely state what the work will be and how it will be divided. The recommendation of the committee is that the association authorize the referee to appoint such associate referees as he may see fit, to take part in this work and make such subdivisions of the subject as may seem best. The committee further earnestly recommends that in view of the scarcity of men to do the work, a special invitation be sent out by the executive committee to induce all food chemists to work along these lines and to joint this association.

On motion of Mr. Leech, the recommendation was adopted.

Mr. MUNSON. I would like to ask what action has been taken on the recommendations of the referee on sugar.

The PRESIDENT. These recommendations have been overlooked. If there is no objection they will be assigned to Committee B, and a report will be written so that action can be taken next year.[a]

Mr. STREET. I am afraid that our committee has made an error in acting on the nitrogen recommendation. Should they have been referred to some other committee? We shall be glad to be instructed by the convention.

The PRESIDENT. It is understood by the association that nitrogen is assigned to Committee A.

Mr. VAN SLYKE. Recommendations on the subject of separation of nitrogenous bodies should be referred to the committee on foods or on dairy products. In the case of the recommendation made on this subject in the paper read yesterday, I move that it be referred to Committee B having charge of diary products.[a]

The motion was adopted.

Mr. LEACH (continuing report on food adulteration). There is one other point that I would like to speak of, and that is the committee on food adulteration has made some slight changes in the provisional methods as printed in Bulletin No. 65, United States Department of Agriculture, Bureau of Chemistry, and it is recommended that these be adopted as part of the provisional methods. This bulletin was discussed and criticised by the food referees, submitted to the association, and adopted last year as provisional, but subsequent experience has dictated certain changes, and we ask that these changes be incorporated in the provisional methods.

Mr. MUNSON. I move the adoption of this recommendation.

The motion was adopted.

The PRESIDENT. I will now call on Mr. Van Slyke for the report of the committee on resolutions.

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[a] As these references were made shortly before adjournment, action was deferred on the recommendations until the meeting of 1903, when the report of chairman of Committee B will be completed.

REPORT OF COMMITTEE ON RESOLUTIONS.

Mr. VAN SLYKE. No resolutions have been reported to the convention, but as chairman I take the responsibility of submitting the usual resolutions which are presented at the close of the convention:

Resolved, That we extend to the Secretary of Agriculture our hearty thanks for the continued assistance which he has so generously given to this association.

Resolved, That we acknowledge the courtesy of the authorities of the Columbian University, and thank them for giving us the use of this room for holding the sessions of our convention.

Resolved, That a committee of three be appointed as referees to take charge of the work relating to separation of nitrogenous compounds, the work to be distributed among the members of the committee on the following lines of division: (1) Meat proteids; (2) vegetable proteids; (3) milk and cheese proteids.

These resolutions were adopted.

Mr. WILEY. I move that we offer a resolution of thanks to the president of this association for the impartial manner in which he has conducted this convention.

The motion prevailed.

At 11.30 a. m. the convention adjourned sine die.

17261—No. 73—03——12

OFFICERS, REFEREES, AND COMMITTEES OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS FOR THE YEAR 1903.

PRESIDENT.

Mr. R. J. DAVIDSON, Blacksburg, Va.

VICE-PRESIDENT.

Mr. M. E. JAFFA, Berkeley, Cal.

SECRETARY.

Mr. H. W. WILEY, Washington, D. C.

ADDITIONAL MEMBERS OF EXECUTIVE COMMITTEE.

Mr. C. L. PENNY, Newark, Del.
Mr. A. E. LEACH, Boston, Mass.

REFEREES.

Phosphoric acid: B. H. Hite, Morgantown, W. Va.
Nitrogen:
Determination of nitrogen: Fred W. Morse, Durham, N. H.
Separation of nitrogenous bodies (milk and cheese proteids): L. L. Van Slyke, Geneva, N. Y.
Potash: F. B. Carpenter, Richmond, Va.
Soils: F. P. Veitch, Washington, D. C.
Dairy products: George Cavanaugh, Ithaca, N. Y.
Foods and feeding stuffs: F. D. Fuller, Geneva, N. Y.
Sugar: G. L. Spencer, Washington, D. C.
Tannin: George A. Kerr, Damascus, Va.
Insecticides: J. K. Haywood, Washington, D. C.
Ash: G. S. Fraps, Raleigh, N. C.

ASSOCIATE REFEREES.

Phosphoric acid: C. B. Williams, Raleigh, N. C.
Nitrogen:
Determination of nitrogen: Edward B. Holland, Amherst, Mass.
Separation of nitrogenous bodies:
Vegetable proteids: R. Harcourt, Guelph, Canada.
Meat proteids: W. D. Bigelow, Washington, D. C.
Potash: M. G. Donk, Tallahassee, Fla.
Soils: C. C. Moore, Washington, D. C.
Dairy products: G. E. Patrick, Washington, D. C.
Foods and feeding stuffs: L. H. Smith, Urbana, Ill.

Food adulteration:

(1) Colors: A. S. Mitchell, Milwaukee, Wis.
(2) Saccharine products, including confectionery: Elton Fulmer, Pullman, Wash.
(3) Fruit products: L. S. Munson, Washington, D. C.
(4) Wine: Geo. E. Colby, Berkeley, Cal.
(5) Beer: H. E. Barnard, Concord, N. H.
(6) Distilled liquors: C. A. Crampton, Washington, D. C.
(7) Vinegar: W. M. Allen, Raleigh, N. C.
(8) Flavoring extracts: A. L. Winton, New Haven, Conn.
(9) Spices: R. E. Doolittle, Lansing, Mich.
(10) Baking powder and baking chemicals: F. T. Green, San Francisco, Cal.
(11) Meat and fish: M. E. Jaffa, Berkeley, Cal.
(12) Fats and oils: L. M. Tolman, Washington, D. C.
(13) Dairy products: A. E. Leach, Boston, Mass.
(14) Cereal products: A. McGill, Ottawa, Canada.
(15) Infants' and invalids' foods: H. W. Wiley, Washington, D. C.
(16) Vegetables: G. W. Cavanaugh, Ithaca, N. Y.
(17) Condiments (other than spices): J. O. La Bach, Lexington, Ky.
(18) Cocoa and cocoa products: E. N. Eaton, Chicago, Ill.
(19) Tea and coffee: W. H. Ellis, Toronto, Canada.
(20) Preservatives: W. D. Bigelow, Washington, D. C.

Sugar:

Optical methods: L. M. Tolman, Washington, D. C.
Chemical methods: L. S. Munson, Washington, D. C.
Special analytical methods used in the sugar industry: David L. Davoll, Caro, Mich.

Tannin: H. C. Reed, Stamford, Conn.
Insecticides: James Emery, Washington, D. C.
Ash: F. T. Shutt, Ottawa, Canada.

COMMITTEE ON FOOD STANDARDS.

Mr. Wm. Frear, State College, Pa., chairman.
Mr. H. W. Wiley, Washington, D. C.
Mr. H. A. Weber, Columbus, Ohio.
Mr. M. A. Scovell, Lexington, Ky.
Mr. E. H. Jenkins, New Haven, Conn.

COMMITTEE ON FERTILIZER LEGISLATION.

Mr. H. W. Wiley, Washington, D. C., chairman.
Mr. B. W. Kilgore, Raleigh, N. C.
Mr. H. B. McDonnell, College Park, Md.
Mr. H. A. Huston, Lafayette, Ind.
Mr. B. B. Ross, Auburn, Ala.

CONSTITUTION OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS.

(1) This association shall be known as the Association of Official Agricultural Chemists of the United States. The objects of the association shall be (1) to secure uniformity and accuracy in the methods, results, and modes of statement of analysis of fertilizers, soils, cattle foods, dairy products, and other materials connected with agricultural industry; (2) to afford opportunity for the discussion of matters of interest to agricultural chemists.

(2) Analytical chemists connected with the United States Department of Agriculture, or with any State or national agricultural experiment station or agricultural college, or with any State or national institution or body charged with official control of the materials named in section 1, shall alone be eligible to membership; and one such representative for each of these institutions or boards, when properly accredited, shall be entitled to enter motions or vote in the association. Only such chemists as are connected with institutions exercising official fertilizer control shall vote on questions involving methods of analyzing fertilizers. All persons eligible to membership shall become members ex officiis and shall be allowed the privileges of membership at any meeting of the association after presenting proper credentials. All members of the association who lose their right to such membership by retiring from positions indicated as requisite for membership shall be entitled to become honorary members and to have all privileges of membership save the right to hold office and vote. All analytical chemists and others interested in the objects of the association may attend its meetings and take part in its discussions, but shall not be entitled to enter motions or vote.

(3) The officers of the association shall consist of a president, a vice-president, and a secretary, who shall also act as treasurer; and these officers, together with two other members to be elected by the association, shall constitute the executive committee. When any officer ceases to be a member by reason of withdrawing from a department or board whose members are eligible to membership, his office shall be considered vacant, and a successor may be appointed by the executive committee, to continue in office till the annual meeting next following.

(4) There shall be appointed by the executive committee, at the regular annual meeting, a referee and such associate referees for each of the subjects to be considered by the association as that committee may deem appropriate.

It shall be the duty of these referees to prepare and distribute samples and standard reagents to members of the association and others desiring the same, to furnish blanks for tabulating analyses, and to present at the annual meeting the results of work done, discussion thereof, and recommendations of methods to be followed.

(5) The special duties of the officers of the association shall be further defined, when necessary, by the executive committee.

(6) The annual meeting of this association shall be held at such place as shall be decided by the association, and at such time as shall be decided by the executive committee, and announced at least three months before the time of meeting.

(7) No changes shall be made in the methods of analysis used in official inspection, except by unanimous consent, until an opportunity shall have been given all official chemists having charge of the particular inspection affected to test the proposed changes.

(8) Special meetings shall be called by the executive committee when in its judgment it shall be necessary, or on the written request of five members; and at any meeting, regular or special, seven enrolled members entitled to vote shall constitute a quorum for the transaction of business.

(9) The executive committee will confer with the official boards represented with reference to the payment of expenses connected with the meetings and publication of the proceedings of the association.

(10) All proposed alterations or amendments to this constitution shall be referred to a select committee of three at a regular meeting, and after report from such committee may be adopted by the approval of two-thirds of the members present entitled to vote.

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